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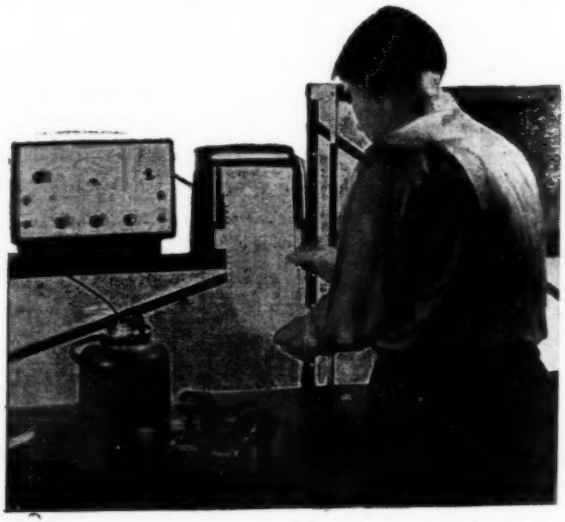

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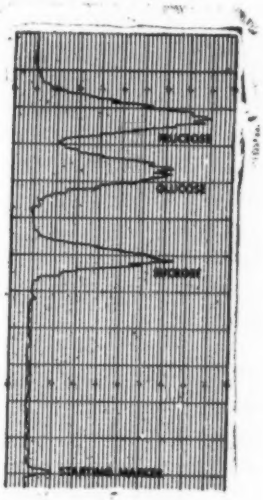

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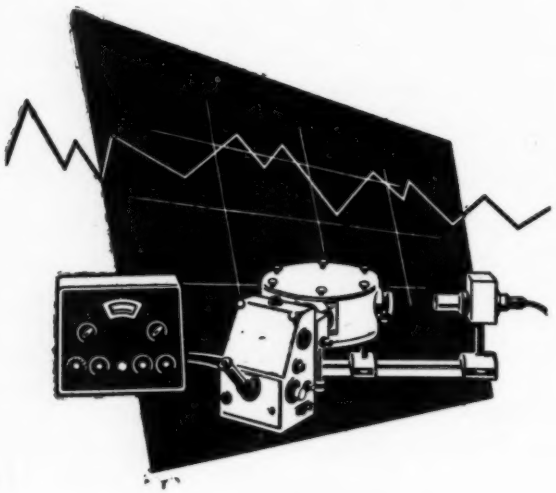

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HYDROXY- AND ALKOXY-ALKYLBIGUANIDE METAL COMPLEXES. PART I. COPPER COMPLEXES

By Nihar Ranjan Sengupta and Priyadaranjan Rây*

Complex compounds of hydroxy-alkylbiguanides (ethanol-, propanol- and *iso*propanol-biguanide) and alkoxyalkylbiguanides (methoxyethyl- and methoxypropyl-biguanide) with copper (II) have been prepared and their properties studied with a view to investigating the influence of the hydroxyl or alkoxyl group in the substituted alkylbiguanides on their chelating capacities. In the case of copper complexes, the position of the hydroxyl group in the ligand has been found to influence its complexing power; this is illustrated by the isolation of a series of deep blue (like ultramarine) diol-binuclear copper complexes.

Four different types of complexes, namely, copper *bis*-hydroxy (or alkoxy)-alkylbiguanide, diol-di-copper di-ethanol (or *iso*propanol)-biguanide, copper *mono*-ethanolbiguanide and oxy-di-copper di-prodanolbiguanide, differing in colour and solubility, have been obtained.

The magnetic moment values (μ_B = 1.65 to 1.86) of these coloured copper compounds indicate that they belong to the inner-metallic planar square penetration type of complexes with dsp^2 hybrid bonds.

Biguanide and substituted biguanides as complexing ligands have revealed many new facts and phenomena of considerable significance to the co-ordination chemistry. Rây and coworkers (this *Journal*, 1950, **27**, 493, 619; 1952, **29**, 157, 217; 1956, **33**, 841; 1958, **35**, 595, 601) have observed that the property and stability of metal biguanide complexes vary with the nature of the substituent (alkyl or aryl) in the ligand molecule. The metal complexes of substituted alkylbiguanides have not been studied except in one or two cases as complexing ligands. This applies particularly to the substituted alkylbiguanides like hydroxy- or alkoxy-alkylbiguanides. The present work records an account of the preparation and properties of the copper complexes of some of these chelating ligands.

The only hydroxyalkylbiguanide described in the literature is ethanolbiguanide (Slotta and Tschesche, *Ber.*, 1929, **62**, 1390) which was synthesised from guanyl-*s*-ethylthiourea hydrobromide and ethanolamine. It has been found, however, that a large number of hydroxy- and alkoxy-alkylbiguanides can be easily obtained by the interaction of the hydroxy- or alkoxy-amines with dicyandiamide in boiling aqueous solution in the presence of copper sulphate, when the sulphate of the corresponding complex copper biguanide separates as a precipitate. From the complex copper compounds, the corresponding biguanide sulphates were obtained by the removal of copper as copper sulphide. In this way, ethanol-, propanol-, *iso*propanol- (in solution), methoxyethyl- and methoxypropyl-biguanides have been prepared.

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A series of complex rose-violet copper *bis*-biguanide compounds, which-comprise those of ethanol-, propanol-, *iso*propanol-, methoxyethyl- and methoxypropyl- biguanides, in the form of sulphate, chloride, bromide, iodide, nitrate, nitrite, carbonate, thiosulphate, dithionate, etc., besides their complex bases, have been prepared and their properties studied. All these compounds are more soluble than those derived from the simple biguanide and alkylbiguanides. Some of these are also soluble in alcohol. An account of their formation and stability studied by *p*H measurements in solution will be reported in a separate communication.

Copper *bis*-ethanol- and *bis-iso*propanol-biguanide salts suffer hydrolysis in boiling aqueous solution or suspension, giving rise to deep blue (like ultramarine) insoluble crystalline compounds. These can be represented as binuclear diol compounds from their composition and properties:

$$\left[\text{(s—BigH).Cu}\begin{matrix}\nearrow \text{OH} \searrow \\ \nwarrow \text{HO} \swarrow\end{matrix}\text{Cu (s—BigH)} \right] X_2;$$

where s-BigH = ethanol- or *iso*propanolbiguanide and X = any univalent anion or an equivalent of polyvalent anion.

These can also be obtained directly by refluxing for a long time an aqueous solution of dicyandiamide and the corresponding amine (ethanol- or *iso*propanol-amine) in the presence of copper sulphate. The diol compounds are decomposed by treatment with alkali solutions into the rose-violet *bis*-biguanide complex with separation of copper hydroxide:

$$\left[\text{(s—BigH).Cu}\begin{matrix}\nearrow \text{OH} \searrow \\ \nwarrow \text{HO} \swarrow\end{matrix}\text{Cu.(s—BigH)} \right] X_2 + 2\text{NaOH}$$

$$= [\text{Cu(s—BigH)}_2]\,(\text{OH})_2 + 2\text{NaX} + \text{Cu(OH)}_2.$$

On adding ammonia to an aqueous suspension of diol complexes and then saturating it with ammonium sulphate, the rose-violet copper *bis*-hydroxyalkylbiguanide sulphate can be obtained.

A light blue, moderately soluble complex copper *mono*-ethanolbiguanide sulphate has been obtained by the gradual addition of an acid to the rose-violet copper *bis*-ethanolbiguanide sulphate (*p*H 4.0 to 4.5). The reaction may be represented as:

$$[\text{Cu(s—BigH)}_2]\,X_2 + H_2SO_4 + 2H_2O = [\text{Cu(s—BigH)}(H_2O)_2]\,X_2 + \text{(s—BigH)}.\,H_2SO_4.$$

The complex copper *mono*-ethanolbiguanide chloride is extremely soluble in water and suffer dismutation on warming, giving rise to an equilibrium in solution as shown below. On adding an alkali salt to this solution, the corresponding rose-violet complex copper *bis*-ethanolbiguanide salt is precipitated and a simple copper salt remains in solution:

$$2\,[\text{Cu (s—BigH)}\,(H_2O)_2]\,Cl_2 \rightleftharpoons [\text{Cu(s—BigH)}_2]\,Cl_2 + CuCl_2 + 4H_2O$$

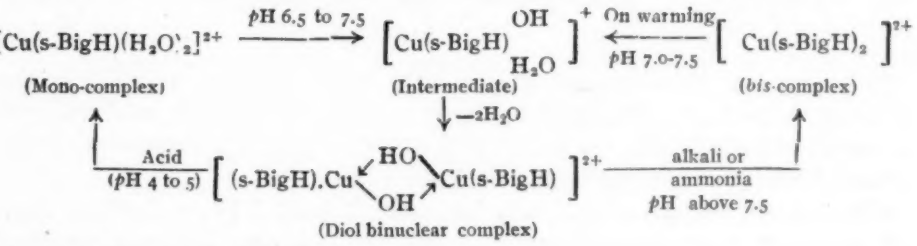
$$\downarrow 2\text{NaX}$$

$$[\text{Cu(s—BigH)}_2]\,X_2 + 2\text{NaCl}$$

(X = thiosulphate, chromate, nitrate, bromide, etc.).

Complex copper *mono*-biguanide salts of any other hydroxy- and alkoxy-alkyl-biguanide could not be isolated as their formation is restricted within a narrow *p*H range (*p*H ~5).

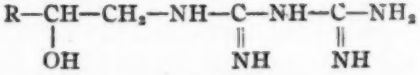
The aqueous solution of the complex copper *mono*-ethanolbiguanide, when neutralised with alkali (*p*H 6 to 7), turns deep blue, from which deep blue crystals of the corresponding binuclear diol copper complex gradually separate out. Hence, the diol binuclear copper biguanide complex occupies an intermediate position between the corresponding *mono*-biguanide and *bis*-biguanide complexes, depending on the *p*H value of the solution. At *p*H 4 to 5 the *mono*-biguanide complex, at *p*H 6.5 to 7.5 the diol binuclear complex and at *p*H above 7.5 the *bis*-biguanide complex become stable. Hence the mechanism of formation of the diol complex may be represented as:



where s-BigH = ethanolbiguanide.

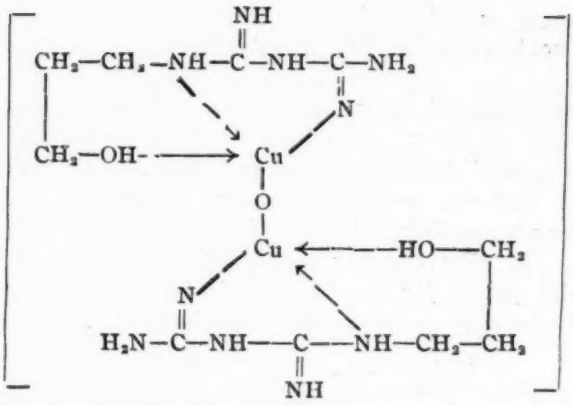
Thus, besides the usual stepwise change from copper *mono*-ethanolbiguanide to copper *bis*-ethanolbiguanide complex or *vice versa*, a side hydrolytic reaction takes place at *p*H 6.5 to 7.5 leading to the formation of a diol binuclear copper ethanolbiguanide complex. Similar behaviour is also shown by the copper *iso*propanolbiguanide complexes.

In the case of alkylbiguanide or alkoxy-alkylbiguanide copper complexes, however, the formation of such intermediate binuclear diol complexes has not been observed. This seems to suggest that the specific character of the substituent hydroxy-alkyl group is responsible for the formation of these diol binuclear copper biguanide complexes. Then again, though ethanolbiguanide and *iso*propanolbiguanide give rise to the formation of diol binuclear copper complexes, propanolbiguanide, on the other hand, fails to form such compounds. It may therefore be concluded that the condition essential for the formation of binuclear diol complexes is not only the presence of a hydroxyl group in the substituent but also its occurrence at the carbon atom in β-position to the nitrogen of the substituted amino group of the biguanide molecule, as shown below:



(where R = H or CH_3)

With propanol biguanide, a brick-red crystalline complex copper compound of the composition, CuO.Cu(s-Big)$_2$, has been obtained. This can only be represented by the following configuration:



The complex is stable towards alkali and is decomposed by acids. Ammonium sulphate converts the complex into copper *bis*-propanolbiguanide sulphate. With a requisite amount of acids, the compound is converted into the corresponding complex copper *bis*-propanolbiguanide salt and the simple copper salt:

$$[Cu_2(OH.C_3H_6.Big)_2O] + 2H_2SO_4 = [Cu(OH.C_3H_6.BigH)_2]\,SO_4 + CuSO_4 + H_2O.$$

On the other hand, methoxypropylbiguanide does not form any such compound. The presence of a hydroxyl group seems therefore to be necessary for its formation. Again, with ethanol- or *iso*propanol-biguanide, a compound of this type has not been obtained.

Magnetic measurements indicate that both the diol binuclear copper hydroxyalkylbiguanide salts (dark blue) and the copper *mono*-ethanolbiguanide salts (light blue), as well as the copper *bis*-hydroxy- and alkoxy-alkylbiguanide salts (rose-violet), are all inner-metallic complexes of the penetration type with planar square dsp^2 hybrid bonds. For, they all give a moment value of 1.65 to 1.86 μ_B (Rây and Sen, this *Journal*, 1948, **25**, 473).

EXPERIMENTAL

A. Ethanolbiguanide

Ethanolbiguanide Sulphate.—Ethanolamine (20 g.) and dicyandiamide (16.8 g.) were boiled under reflux in aqueous solution (70 c.c. of water) for an hour. $CuSO_4.5H_2O$ (20 g.) in 50 c.c. of water was added to it in small portions at a time, fresh quantity being introduced as soon as the precipitated copper hydroxide from the previous addition dissolved to give a blue-violet solution. The mixture was then filtered and the filtrate cooled in ice. Rose-violet crystals of the complex copper ethanolbiguanide sulphate separated in quantities. These were filtered and washed with water. The product was then suspended in 100 c.c. of water and into this H_2S was passed till saturation. Precipitated copper sulphide was filtered off and a vigorous current of air was passed through the filtrate to expel the dissolved H_2S. The solution was filtered and the filtrate concentrated in vacuum over sulphuric acid. The concentrated solution was then treated with acetone, when white crystalline

ethanolbiguanide sulphate separated out. The crystals were filtered and dried over $CaCl_2$; m.p. 148°, yield 5 g. [Found: N, 36.12; SO_4, 24.86. $(OH.C_2H_4.C_2N_5H_6)_2.H_2SO_4$ requires N, 36.08; SO_4, 24.74%].

Copper bis-*Ethanolbiguanide Complexes*

1. *Copper* bis-*Ethanolbiguanide Sulphate.*—The crude rose-violet product, obtained as described above, was dissolved in 50 c.c. of 1:4 (by vol.) sulphuric acid in the cold. The solution was filtered and treated with concentrated ammonia till just alkaline. The complex copper compound again separated at once. This was filtered, washed thoroughly with water and then with absolute alcohol. The product was dried in air. {Found: Cu, 11.63; N, 26.23; SO_4, 17.89; H_2O (by loss at 110°), 16.66. $[Cu(OH.C_2H_4.C_2N_5H_6)_2]SO_4.5H_2O$ requires Cu, 11.77; N, 25.95; SO_4, 17.79; H_2O, 16.68%}.

2. *Copper* bis-*Ethanolbiguanide Base.*—The above described complex sulphate (5.39 g.) was triturated in a mortar for about 10 minutes with 3.15 g. of baryta, $Ba(OH)_2.8H_2O$, in 10 c.c. of CO_2-free water to a smooth paste and then taken up with 50 c. c. of CO_2-free water, and the mixture filtered immediately. The filtrate was concentrated to 20 c.c. in vacuum over KOH and $CaCl_2$. From the concentrated solution the rose-coloured complex base was precipitated by the addition of absolute alcohol. This was filtered, washed twice with ice-cold aqueous alcohol (1:4) and then with absolute alcohol. The product was dried over KOH and $CaCl_2$. {Found: Cu, 14.46; N, 31.52. $[Cu(OH.C_2H_4.C_2N_5H_6)_2](OH)_2$, $2.5H_2O$ requires Cu, 14 69; N, 31.63%}.

When heated to a constant weight it loses all its water including the base-forming ones and forms the anhydro-base. {Found: Cu, 18.03; N, 39.96. $[Cu(OH.C_2H_4.C_2N_5H_5)_2]$ requires Cu, 18.06; N, 39.83%}.

The complex copper base is highly soluble in water and almost insoluble in alcohol, acetone, etc. Its aqueous solution reacts alkaline to litmus (*p*H 10.5 to 11.0). It liberates ammonia from ammonium salts and absorbs CO_2 from atmosphere.

3. *Copper* bis-*ethanolbiguanide chloride* was prepared by digesting the complex sulphate (5.39 g.) with a cold concentrated solution of a calculated quantity of barium chloride (2.44 g. of $BaCl_2$, $2H_2O$ in 20 c.c. of water) in a mortar. The filtrate, free from barium and sulphate ions, was concentrated in a vacuum desiccator over concentrated sulphuric acid. The rose-violet complex chloride was precipitated from the solution by the addition of absolute alcohol. The product was washed first with cold aqueous alcohol (1:4 by vol.), then with absolute alcohol and afterwards dried in air. {Found: Cu, 13.36; N, 29.83; Cl, 15.16; H_2O (by loss at 110°), 9.30. $[Cu(OH.C_2H_4.C_2N_5H_6)_2]Cl_2.2H_2O$ requires Cu, 13.52; N, 29.82; Cl, 15.12; H_2O, 9.58%}.

All other salts of copper *bis*-ethanolbiguanide, as noted below, were prepared by adding an aqueous solution of the corresponding alkali salts to that of the complex chloride. These were washed first with cold water, then with absolute alcohol and finally dried in air.

TABLE I

Compound	Found.	Calc
1. Bromide	Cu: 12 02%	12.15%
$[Cu.X_2]Br_2.0.5H_2O$	Br: 30.75	30.62
	H_2O: 1.55	1.75
2. Iodide	Cu: 9.56	9.73
$[Cu.X_2]I_2.2.5H_2O$	I: 39.56	38 94
	H_2O: 6 96	6.89
3. Nitrate	Cu: 12 49	12.39
$[Cu.X_2]\ (NO_3)_2.2H_2O$	N: 32.76	32.75
	NO_3: 24.05	24.15
	H_2O: 6.97	7.31
4. Carbonate	Cu: 14.18	14.13
$[Cu.X_2].CO_3.2H_2O$	N: 31.27	31.14
	H_2O: 8.12	8.02
5. Thiosulphate	Cu: 13.29	13.13
$[Cu\ X_2]\ S_2O_3.H_2O$	S_2O_3: 22.84	23.16
	H_2O: 3.72	3 72
6. Dithionate	Cu: 12.07	11.95
$[Cu.X_2]\ S_2O_6\ H_2O$	S: 11.96	12.04
	H_2O: 3.44	3 39
7. Nitrite	Cu: 12.20	12.48
$[Cu.X_2]\ (NO_2)_2.3.5H_2O$	N: 33.92	33.04
	H_2O: 12.21	12 48
8. Phosphate	Cu: 12 88	12 85
$[Cu.X_2]\ HPO_4.2.5H_2O$	PO_4: 19.01	19.22
	H_2O: 9.55	9.11
9. Arseniate	Cu: 11 44	11.22
$[Cu.X_2]\ HAsO_4.4H_2O$	As: 13.49	13.23
	H_2O: 12 83	12.7[illegible]
10. Chromate	Cu: 12.30	12 14
$[Cu.X_2]\ CrO_4.3H_2O$	CrO_4: 22.21	22.16
	H_2O: 10.03	10.02
11. Acetate	Cu: 11.45	11 49
$[Cu.X_2]\ (CH_3COO)_2.4.5H_2O$	N: 25.74	25.32
	H_2O: 14.43	14.66

$[X = OH.C_2H_4.C_2N_5H_6]$.

Properties.—All the salts of the complex copper base are rose-violet in colour excepting the chromate, due to the colour of its anion which predominates. With the exception of the chloride and acetate, all the salts are more or less sparingly soluble in water. Many of them, e.g. sulphate, chloride, bromide, iodide, dithionate, nitrate and nitrite, when heated with water for a long time, are converted into the corresponding deep blue binuclear diol salts, which are sparingly soluble or almost insoluble in water.

Copper mono-*Ethanolbiguanide Complexes*

1. *Copper* mono-*Ethanolbiguanide Sulphate.*—Copper *bis*-ethanolbiguanide sulphate (10 g.) was dissolved in 100 c.c. of cold $2N$-H_2SO_4. The solution was filtered and the filtrate was treated with dilute ammonia dropwise with constant stirring till the *p*H of the solution became 4 to 4.5. This was then cooled in ice, when the light blue crystals of the complex copper *mono*-ethanolbiguanide sulphate separated from the solution. The crystals were washed first with water, then with absolute alcohol and afterwards dried in air. { Found : Cu, 18.74 ; N, 21.00 ; SO_4, 27.94 ; H_2O (by loss at 130°), 10.49. $[Cu(OH.C_2H_4.C_2N_5H_6)(H_2O)_2]SO_4$ requires Cu, 18.65 ; N, 20.56 ; SO_4, 28.19 ; H_2O, 10.57% }.

The substance is moderately soluble in cold water but insoluble in alcohol. By the action of alkali or ammonia it changes to the rose-violet *bis*-biguanide copper complex with separation of copper hydroxide.

2. *Copper* mono-*Ethanolbiguanide Chloride.*—The complex blue chloride was prepared by double decomposition between the calculated amount of complex sulphate and barium chloride in aqueous solution. The filtrate, freed from barium sulphate, was evaporated in vacuum, when the blue copper *mono*-ethanolbiguanide chloride crystallised out. The crystals were washed successively with aqueous alcohol (1 : 4 by vol.) and absolute alcohol, and then dried in air. { Found : Cu, 20.49 ; N, 22.32 ; Cl, 22.80 ; H_2O (by loss at 130°), 11.12. $[Cu(OH.C_2H_4.C_2N_5H_6)(H_2O)_2]Cl_2$ requires Cu, 20.13 ; N, 22.50 ; Cl, 22.82 ; H_2O, 11.41% }.

The blue crystals of the complex chloride are extremely soluble in water. The aqueous solution shows a *p*H of 5.0 to 5.5. On treating the solution of the complex chloride with alkali salts, the corresponding sparingly soluble salts of the rose-violet copper *bis*-ethanolbiguanide separate out from the solution.

Diol-di-Copper di-Ethanolbiguanide Complexes

1. *Diol-di-Copper di-Ethanolbiguanide Sulphate.*—Dicyandiamide (16.8 g.), ethanolamine (20 g.) and $CuSO_4$, $5H_2O$ (20 g.) in 200 c.c. of water were refluxed for about half an hour. The resulting blue-violet solution was filtered rapidly and the filtrate was again refluxed for 3 to 4 hours. A deep blue (ultramarine colour) sparingly soluble complex copper compound separated from the solution and collected in the reaction flask. The mixture was then filtered. The very sparingly soluble deep blue crystals were collected on the filter bed, washed successively with 50 c.c. of 1% ammoniacal water, 200 c.c. of water and absolute alcohol. The product was dried in air to a constant weight.

The same compound was also obtained by warming an aqueous suspension of copper *bis*-ethanolbiguanide sulphate on the water-bath for 5 to 6 hours. { Found : Cu, 23.42 ; N, 25.66 ; SO_4, 17.66. $[Cu_2(OH.C_2H_4.C_2N_5H_6)_2(OH)_2]SO_4$ requires Cu, 23.21 ; N, 25.59 ; SO_4, 17.54% }.

2. *Diol-di-copper di-ethanolbiguanide chloride* was prepared by warming an aqueous solution of the rose-violet copper *bis*-ethanolbiguanide chloride (2 g. in 100 c.c. of water) on the water-bath for 8 to 10 hours. The product was then filtered, washed

with cold water and dried in air. { Found : Cu, 24.08 ; N, 26.95 ; Cl, 13.84. $[Cu_2(OH.C_2H_4.C_2N_5H_6)_2(OH)_2]Cl_2$ requires Cu, 24.32 ; N, 26.82 ; Cl, 13.60% }.

All the other salts noted below (Table II) were prepared by heating an aqueous-suspension of the corresponding rose-violet *bis*-ethanolbiguanide salts on the water-bath. The product was washed thoroughly first with cold water, then with absolute alcohol, and finally dried in air.

TABLE II

Diol-di-copper di-ethanol-biguanide salts.	Found.	Calc.
1. Bromide	Cu : 20 89%	20.79%
$[Cu_2X_2(OH)_2]Br_2$	Br : 26.65	26.19
2. Iodide	Cu : 18.02	18.01
$[Cu_2X_2(OH)_2]I_2$	I : 36 14	36.04
3. Nitrate	Cu : 22.29	22.09
$[Cu_2X_2(OH)_2](NO_3)_2$	N : 28.60	29.22
4. Nitrite	Cu : 23 63	23.39
$[Cu_2X_2(OH)_2](NO_2)_2$	N : 31.67	30.94
5. Dithionate	Cu : 20.92	20.79
$[Cu_2X_2(OH)_2]S_2O_6$	S : 10.42	10.47
6. Phosphate	Cu : 23.56	23.21
$[Cu_2X_2(OH)_2]HPO_4$	PO_4 : 17.30	17.35
7. Arseniate	Cu : 21.39	21.52
$[Cu_2X_2(OH)_2]HAsO_4$	As : 12.40	12.68

[where $X = OH.C_2H_4.C_2N_5H_6$].

Properties.—The binuclear diol complex copper salts form deep blue crystals, almost insoluble in water. The complex chloride, however, is slightly soluble. On adding alkali or ammonia to their aqueous suspensions, they readily pass into solution as copper *bis*-ethanolbiguanide base with separation of some copper hydroxide. The diol complex is, however, easily decomposed by acids.

B. iso*Propanolbiguanide*

iso*Propanolbiguanide sulphate* was obtained in solution by eliminating copper from the sulphate of its copper complex. The latter was obtained by refluxing dicyandiamide, *iso*propanolamine and copper sulphate by the usual procedure as described before. The *iso*propanolbiguanide sulphate in the pure solid state, however, could not be obtained as its aqueous solution on evaporation even in vacuum yielded only a syrupy mass. This, on keeping, however, lost its characteristic reaction for biguanide. It shows that the *iso*propanolbiguanide sulphate in solution is rather unstable and decomposes on keeping and concentration, due possibly to the formation of *iso*propanolguanylurea by gradual hydrolysis (Rây

and Kundu, *ibid.*, 1952, **29**, 811). However, the freshly prepared solution was found to react as usual with copper and nickel salts. In the prepartion of its metallic complexes, described below, a freshly prepared solution of the *iso*propanol-biguanide sulphate was therefore always employed.

Copper bis-iso*Propanolbiguanide Complexes*

1. *Copper* bis-iso*Propanolbiguanide Sulphate.*—A blue-violet solution was obtained by refluxing dicyandiamide (17 g.), *iso*propanolamine (19 g.) and $CuSO_4.5H_2O$ (17 g.) in 100 c.c. of water for about 3 hours. The solution was cooled in ice, when along with the diol binuclear copper complex, the rose-violet complex copper *bis-iso*propanolbiguanide sulphate crystallised out. The crude material was filtered, washed thoroughly with water and then suspended in 100 c.c. of water. Copper was eliminated as copper sulphide by passing H_2S through the mixture. A vigorous current of air was then passed through the filtrate to remove the dissolved H_2S. The solution was filtered and treated with a solution of ammoniacal copper sulphate (2.5 g. of $CuSO_4.5H_2O$ in 25 c.c. of water), when the rose-violet crystals of complex copper *bis-iso*propanolbiguanide sulphate separated. These were filtered, washed first with water, then with absolute alcohol and finally dried in air. {Found: Cu, 12.00; N, 26.02; SO_4, 18.10; H_2O (by loss at 110°), 10.40. $[Cu(OH.C_3H_6.C_2N_5H_6)_2]SO_4.3H_2O$ requires Cu, 11.95; N, 26.34; SO_4, 18.06; H_2O, 10.16%}.

2. *Copper* bis-iso*propanolbiguanide base* was prepared by triturating in a mortar a calculated amount of the complex sulphate and baryta in 10-15 c.c. of CO_2-free water. The filtrate, freed from barium sulphate, was evaporated to dryness in vacuum over KOH and $CaCl_2$. The dried mass was taken up with absolute alcohol. This was filtered and the filtrate treated with acetone in the cold, when the rose-violet crystals of the complex base separated out. These were filtered, washed with acetone and immediately removed to a desiccator containing KOH and $CaCl_2$ for drying. {Found: Cu, 13.25; N, 29.08; H_2O (by loss at 110°), 14.76. $[Cu(OH.C_3H_6.C_2N_5H_6)_2](OH)_2.4H_2O$ requires Cu, 13.03; N, 28.72; H_2O, 14.77%}.

3. *Copper* bis-iso*Propanolbiguanide Chloride.*—Calculated amounts of the complex sulphate and barium chloride in aqueous solution were triturated in the cold. The filtrate from barium sulphate was evaporated to dryness in vacuum over H_2SO_4. The dried mass was digested with 20 c.c. of absolute alcohol and then filtered. The filtrate was treated with acetone when the crystals of the complex chloride separated from the solution. These were filtered, washed with acetone and dried over $CaCl_2$. {Found: Cu, 12.48; N, 28.11; Cl, 14.27; H_2O (by loss at 110°), 10.18. $[Cu(OH.C_3H_6.C_2N_5H_6)_2]Cl_2.3H_2O$ requires Cu, 12.56; N, 27.70; Cl, 14.05; H_2O, 10.44%}.

All other salts of the series were prepared by adding an aqueous solution of the corresponding alkali salts to that of the complex chloride. These were washed with cold water and dried in air.

TABLE III

Compound.	Found.	Calc.	Compound.	Found.	Calc.
1. Bromide $[Cu.X_2]Br_2.1.5H_2O$	Cu : 11.27%	11.17%	6. Dithionate $[Cu.X_2]S_2O_6.H_2O$	Cu : 11.65%	11.35%
	Br : 28.45	28.15		S : 11.59	11.44
	H_2O : 4.84	4.75		H_2O : 3.44	3.42
2. Iodide $[Cu.X_2]I_2.2H_2O$	Cu : 9.37	9.46	7. Nitrite, $[Cu.X_2](NO_2)_2.5H_2O$	Cu : 11.13	11.35
	I : 38.12	37.83		N : 30.38	30.04
	H_2O : 5.30	5.36		H_2O : 16.19	16.46
3. Nitrate $[Cu.X_2](NO_3)_2.4H_2O$	Cu : 10.72	10.97	8. Phosphate, $[Cu.X_2]HPO_4.3H_2O$	Cu : 11.80	11.95
	N : 29.52	29.09		PO_4 : 17.80	17.87
	H_2O : 12.69	12.46		H_2O : 10.07	10.16
4. Carbonate $[Cu.X_2]CO_3.4H_2O$	Cu : 12.44	12.37	9. Chromate, $[Cu.X_2]CrO_4.3H_2O$	Cu : 11.54	11.51
	N : 27.04	27.27		CrO_4 : 21.36	21.03
	H_2O : 13.94	14.03		H_2O : 10.01	9.76
5. Thiosulphate $[Cu.X_2]S_2O_3.3H_2O$	Cu : 11.91	11.61			
	S_2O_3 : 20.60	20.45			
	H_2O : 10.19	9.86			

[where $X = OH.C_3H_5.C_2N_5H_6$].

Properties.—With the exception of the chloride and the base, which are extremely soluble in water and alcohol, all other complex copper *bis-iso*propanolbiguanide compounds are moderately soluble in water. All these complex salts, excepting the bromide and chromate, are rose-violet in colour. The complex bromide, however, is blue-violet and chromate is dirty yellow. Many of the salts, e.g., sulphate, chloride, bromide, iodide, nitrate, nitrite, etc., when heated with water on the water-bath, give rise to the sparingly soluble, deep blue corresponding binuclear diol copper salts. All the complex copper *bis-iso*propanolbiguanide salts are fairly soluble in ammonia and readily in alkalies.

*Diol-di-Copper di-*iso*Propanolbiguanide Complexes*

1. *Diol-di-Copper di-*iso*Propanolbiguanide Sulphate.*—Dicyandiamide (17 g.) and *iso*propanolamine (19 g.) in 60 c.c. of water were boiled under reflux for about half an hour, when a solution of copper sulphate (20 g. of $CuSO_4.5H_2O$ in 50 c.c. of water) was added in small portions at a time. The remaining procedure was identical with that employed for the preparation of the corresponding ethanol-biguanide compound ; yield 10 g. (approx).

The same compound was also obtained by heating an aqueous suspension of copper *bis-iso*propanolbiguanide sulphate on the water-bath for 8 to 10 hours. {Found : Cu, 22.07 ; N, 24.79 ; SO_4, 16.97. $[Cu_2(OH.C_3H_6.C_2N_5H_6)_2(OH)_2]SO_4$ requires Cu, 22.08 ; N, 24.36 ; SO_4, 16.70%}.

2. *Diol-di-copper di-*iso*propanolbiguanide chloride* was prepared by heating an aqueous solution of the copper *bis-iso*propanolbiguanide chloride (1 g. in 100 c.c. of water) on the water-bath for about 4 to 5 hours. The crystals that separated were filtered, washed first with cold water, then with absolute alcohol and finally dried in air. {Found : Cu, 21.68 ; N, 24.07 ; Cl, 11.90 ; H_2O (by loss at 90°), 6.20. $[Cu_2(OH.C_3H_6.C_2N_5H_6)_2(OH)_2]Cl_2.2H_2O$ requires Cu, 21.67 ; N, 23.89 ; Cl, 12.12 ; H_2O, 6.14%}.

All other salts of the series, as tabulated below, were prepared by heating an aqueous suspension of the corresponding *bis*-biguanide salts on the water-bath for 6 to 8 hours. The products were washed and dried as usual.

TABLE IV

Compound.	Found.	Calc.
1. Bromide	Cu : 20.16 %	19.86%
$[Cu_2.X_2.(OH)_2]Br_2$	Br : 25.42	25.04
2. Iodide	Cu : 17.25	17.32
$[Cu_2.X_2.(OH)_2]I_2$	I : 34.89	34.64
3. Nitrate	Cu : 20.47	20.45
$[Cu_2.X_2.(OH)_2](NO_3)_2.H_2O$	N : 26.98	27.05
4. Nitrite	Cu : 21.38	21.56
$[Cu_2.X_2.(OH)_2](NO_2)_2.H_2O$	N : 28.67	28.52

$[X = OH.C_3H_6.C_2N_5H_6]$.

Properties.—The diol binuclear copper *bis-iso*propanolbiguanide salts are deep blue in colour and almost insoluble in water. On adding alkali to the aqueous suspension of the complex, no change was observed, but when warmed on the water-bath, it changed immediately to copper *bis-iso*propanolbiguanide base with the separation of some copper hydroxide. The compounds, however, decompose somewhat on heating at 130°.

C. *Propanolbiguanide*

Propanolbiguanide Sulphate.—Dicyandiamide (8 g.), propanolamine (8 g.) and $CuSO_4.5H_2O$ (6 g.) in 100 c.c. of water were refluxed for 45 minutes. The resulting violet solution was treated with a strong solution of ammonium sulphate, when the crystals of rose-violet copper *bis*-propanolbiguanide sulphate separated at once. The product was filtered, washed thoroughly with water and then suspended in 50 to 60 c.c. of water. Copper was removed by H_2S. The filtrate from CuS was freed of H_2S by air current. The solution was filtered and treated with acetone in the cold. Snow-white crystals of the propanolbiguanide sulphate separated out. These were filtered, washed with acetone and dried over $CaCl_2$; m.p. 170° ± 1°, yield 5 g. {Found : N, 33.83 ; SO_4, 23.24. $(OH.C_3H_6.C_2N_5H_6)_2.H_2SO_4$ requires N, 33.65 ; SO_4, 23.08%}.

1. *Oxy-di-Copper di-Propanolbiguanide* (*Anhydrobase*).—The clear violet-red solution, obtained from dicyandiamide, propanolamine and copper sulphate, as described above, was filtered and the filtrate was refluxed for another half an hour when a brick-red crystalline compound collected in the reaction flask. The crystals were filtered, washed first thoroughly with water, then with absolute alcohol and finally dried over KOH and $CaCl_2$; yield 1 g. {Found: Cu, 27.71 ; N, 30.72 ; C, 27.13 ; H, 5.15. $[Cu_2(OH.C_3H_6.C_2N_5H_5)_2.O]$ requires Cu, 27.67 ; N, 30.50 ; C, 26.14 ; H, 5.23%}.

The substance is insoluble in water or alcohol. The moist compound reacts strongly alkaline to litmus, liberates ammonia from ammonium salts with the separation of the corresponding sparingly soluble copper *bis*-propanolbiguanide

salts. It absorbs both moisture and CO_2 from the atmosphere. The compound is readily decomposed by acids, but is not easily affected by alkalies.

Copper bis-*Propanolbiguanide Complexes*

1. *Copper* bis-*Propanolbiguanide Sulphate*.—A sparingly soluble rose-violet copper *bis*-propanolbiguanide sulphate was obtained by mixing a solution of propanolbiguanide sulphate (6 g. dissolved in 29 c.c. of water containing 10-15 c.c. of dilute ammonia) and $CuSO_4.5H_2O$ (2.5 g. in 10-15 c.c. of water) in the cold. The product was filtered and washed as usual and then dried in air. {Found: Cu, 11.55; N, 25.83; SO_4, 17.28; H_2O (by loss at 110°), 13.40. $[Cu(OH.C_3H_6.C_2N_5H_6)_2]SO_4.4H_2O$ requires Cu, 11.58; N, 25.57; SO_4, 17.53; H_2O, 13.19%}.

2. *Copper* bis-*Propanolbiguanide Base*.—The complex sulphate (1 g.) was treated with 10% caustic alkali solution, when a clear red-violet solution was obtained. This was filtered rapidly and the filtrate warmed on the water-bath for about 10-15 minutes, when the complex copper base separated in the form of rose-red crystals. These were filtered, washed first with water, then with alcohol and finally dried over KOH and $CaCl_2$. {Found: Cu, 16.35; N, 36.48; H_2O (by loss at 110°), 2.22. $[Cu(OH.C_3H_6.C_2N_5H_5)_2].0.5H_2O$ requires Cu, 16.34; N, 36.04; H_2O, 2.32%}.

3. *Copper* bis-*propanolbiguanide chloride* was prepared as usual from the complex sulphate by digesting it with the calculated amount of barium chloride solution. The filtrate from barium sulphate was evaporated to dryness in vacuum over H_2SO_4. The product was taken up with absolute alcohol and from the solution the complex chloride was precipitated by acetone. The product was filtered and dried over $CaCl_2$. {Found: Cu, 13.96; N, 30.35; Cl, 16.07. $[Cu(OH.C_3H_6.C_2N_5H_6)_2]Cl_2$ requires Cu, 14.03; N, 30.94; Cl, 15.69%}.

All other salts of the complex copper *bis*-propanolbiguanide, tabulated below, were obtained as precipitates by adding an aqueous solution of the corresponding alkali salts to that of the complex chloride.

TABLE V

Compound.	Found	Calc.
1. Nitrate	Cu: 11.87%	11.71%
$[Cu.X_2](NO_3)_2.2H_2O$	N: 30.93	31.02
	H_2O: 6.67	6.65
2. Thiosulphate	Cu: 11.63	11.58
$[Cu.X_2]S_2O_3.3H_2O$	S_2O_3: 22.38	22.14
	H_2O: 10.07	9.88
3. Dithionate	Cu: 11.41	11.35
$[Cu.X_2]S_2O_6.H_2O$	S: 11.68	11.44
	H_2O: 3.17	3.27
4. Chromate	Cu: 11.35	11.15
$[Cu.X_2]CrO_4.4H_2O$	CrO_4: 20.14	20.37
	H_2O: 12.58	12.64
5. Phosphate	Cu: 12.18	12.15
$[Cu.X_2]HPO_4.2.5H_2O$	PO_4: 18.08	18.18
	H_2O: 8.32	8.61

[X = $OH.C_3H_6.C_2N_5H_6$

Properties.—With the exception of the complex chloride all the other salts, as also the complex base, are sparingly soluble in cold water. The complex chloride is soluble in water and alcohol, but insoluble in acetone. All these salts excepting the complex chromate, which is dirty yellow, are rose-violet in colour. The moist complex base is strongly alkaline to litmus, liberates ammonia from ammonium salts and absorbs CO_2 from the atmosphere.

D. Methoxyethylbiguanide

Methoxyethylbiguanide Sulphate.—The rose-red copper *bis*-methoxyethylbiguanide sulphate separated as a crystalline solid on refluxing for about half an hour a solution of dicyandiamide (17 g.), methoxyethylamine (20 g.) and $CuSO_4.5H_2O$ (20 g.) in 100-150 c.c. of water. The crude product was then dissolved in $6N$-H_2SO_4 and the solution was saturated with H_2S. The precipitated copper sulphide was filtered off and from the filtrate H_2S was removed by passing a current of air. From the solution, on treatment with absolute alcohol, an oily substance separated. On keeping the mixture in a refrigerator for several days (about 15 days), the oil solidified into crystals. These crystals were filtered, washed with alcohol and dried over $CaCl_2$; yield 12 g; m.p. 180° ± 2°. { Found: N, 24.39; SO_4, 33.76; H_2O (by loss at 100°), 9.46. $(CH_3O.C_2H_4.C_2N_5H_6).H_2SO_4$, $1.5H_2O$ requires N, 24.64; SO_4, 33 80; H_2O, 9.51% }.

Copper bis-*Methoxyethylbiguanide Complexes*

Copper bis-*Methoxyethylbiguanide Sulphate.*—A solution of $CuSO_4.5H_2O$ (2.5 g. in 10 c. c. of water) was mixed with that of methoxyethylbiguanide sulphate (10 g. in 20 c c. of water) and the mixed solution was rendered alkaline by dilute ammonia. Rose-red crystals of the complex sulphate separated at once from the solution. These were filtered, washed first thoroughly with water, then with absolute alcohol and finally dried in air. { Found: Cu, 12.78; N, 28.30; SO_4, 19.21; H_2O (by loss at 110°), 3.44. $[Cu(CH_3O.C_2H_4.C_2N_5H_6)_2]SO_4.H_2O$ requires Cu, 12.81; N, 28 26; SO_4, 19.37; H_2O, 3.63% }.

Copper bis-*methoxyethylbiguanide base* was prepared by digesting the complex sulphate with a calculated amount of baryta solution. The filtrate from barium sulphate was evaporated to dryness and the mass was taken up with absolute alcohol. The rose-coloured complex base was precipitated from the alcoholic solution by acetone. This was filtered, washed with acetone and dried over KOH and $CaCl_2$. { Found: Cu, 14.95; N, 32.66; H_2O (by loss at 110°), 2.32. $[Cu(CH_3O.C_2H_4.C_2N_5H_6)_2](OH)_2.0.5H_2O$ requires Cu, 14.96; N, 32.96; H_2O, 2.12% }.

The *chloride* was prepared by digesting the complex sulphate with the calculated quantity of a barium chloride solution. The filtrate was evaporated to dryness and the mass was taken up with absolute alcohol. The complex chloride separated from the alcoholic solution by the addition of acetone as a rose-red precipitate. This was filtered, washed with acetone and dried over $CaCl_2$. { Found: Cu, 13.57; Cl, 15.35; H_2O (by loss at 110°), 1.92. $[Cu(CH_3O.C_2H_4.C_2N_5H_6)_2]Cl_2.0.5H_2O$ requires Cu, 13.76; Cl, 15.38; H_2O, 1.95% }.

The *nitrate* was obtained from the complex chloride and potassium nitrate by metathesis in solution as a rose-red crystalline precipitate. The substance is sparingly soluble in water. { Found : Cu, 11.85 ; H_2O, 5.12. $[Cu(CH_3O.C_2H_4.C_2N_5H_6)_2]$-$(NO_3)_2.1.5H_2O$ requires Cu, 11.92 ; H_2O, 5.07% }.

E. Methoxypropylbiguanide

Methoxypropylbiguanide Sulphate.—The rose-red copper *bis*-methoxypropylbiguanide sulphate separated as a solid mass on refluxing a solution of dicyandiamide (17 g.), methoxypropylamine (25 g.) and $CuSO_4.5H_2O$ (20 g.) in 50 c.c. of water for about half an hour. From this crude product the *sulphate* was obtained in the pure state by following the procedure already described for methoxyethylbiguanide sulphate ; m.p. 179° ± 1°, yield 10 g. { Found : N, 25.88; SO_4, 35.51. $(CH_3O.C_3H_6.C_2N_5H_6)H_2SO_4$ requires N, 25.83 ; SO_4, 35.42% }.

Copper bis-*Methoxypropylbiguanide Complexes*

1. *Copper* bis-*Methoxypropylbiguanide Sulphate.*—A solution of copper sulphate (2.5 g. in 10 c.c. of water) was mixed with that of methoxypropylbiguanide sulphate (10 g. in 20 c.c. of water) and the mixture was rendered alkaline by dilute ammonia. Rose-coloured crystals of the complex sulphate separated at once. These were filtered, washed first with water, then with absolute alcohol and finally dried in air. { Found : Cu, 12.21 ; N, 26.98 ; SO_4, 18.80 ; H_2O (by loss at 110°), 1.79. $[Cu(CH_3O.C_3H_6.C_2N_5H_6)_2]SO_4.0.5H_2O$ requires Cu, 12.34 ; N, 27.20 ; SO_4, 18.67 ; H_2O, 1.75% }.

2. *Copper* bis-*methoxypropylbiguanide base* was prepared by digesting the complex sulphate with 10% caustic alkali solution on the water-bath. The rose coloured product was filtered, washed with water and dried over KOH and $CaCl_2$. The compound is sparingly soluble in water and its aqueous suspension reacts alkaline to litmus. { Found : Cu, 15.33 ; N, 34.24 ; H_2O (by loss at 110°), 1.97. $[Cu(CH_3O.C_3H_6.C_2N_5H_6)_2]$. $0.5H_2O$ requires Cu, 15.25 ; N, 33.61 ; H_2O, 2.16% }.

3. The *chloride* was obtained by digesting the complex sulphate with an aqueous solution of barium chloride in calculated quantity. The filtrate from barium sulphate was concentrated in vacuum and the rose-coloured complex chloride was precipitated by acetone. The product was filtered, washed with acetone and dried over $CaCl_2$. { Found : Cu, 13.34 ; Cl, 14.98. $[Cu(CH_3O.C_3H_6.C_2N_5H_6)_2]Cl_2$ requires Cu, 13.22 ; Cl, 14.78% }.

4. The *nitrate* was prepared from a solution of the complex chloride by the action of potassium nitrate. It forms rose coloured crystals, sparingly soluble in water. { Found : Cu, 11.32 ; H_2O (by loss at 110°), 3.32. $[Cu(CH_3O.C_3H_6\ C_2N_5H_6)_2]\ (NO_3)_2.$-$H_2O$ requires Cu, 11.52 ; H_2O, 3.26% }.

Method of Analysis

Copper, in the complex, was determined iodometrically after decomposing it with acids. Nitrogen was estimated by Duma's method (semi-micro) and the anions by the usual standard procedures.

Magnetic Susceptibility

The magnetic susceptibility of the compounds was measured following Gouy's method. The results are recorded in Table VI.

TABLE VI

Temp. = 32° (305°A)

	Substance.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	Dia. $\times 10^6$. (corr.)	$\chi_A \times 10^6$.	μ_B.
1.	Cu-*mono*-ethanol-B (anhydrous)	3.072	1046	125	1171	1.70
2.	Cu-*bis*-ethanol-B (pentahydrate)	2.087	1127	223	1350	1.82
3.	Diol-di-Cu di-ethanol-B (anhydrous)	4.113	1125	93	1218	1.73
4.	Diol-di-Cu di-*iso*propanol-B (anhydrous)	3.539	1028	105	1133	1.67
5.	Cu *bis-iso*propanol-B (trihydrate)	1.926	1023	200	1223	1.74
6.	Cu *bis*-propanol-B (tetrahydrate)	1.805	988	247	1235	1.75
7.	Cu *bis*-methoxyethyl-B (monohydrate)	2.480	1229	190	1419	1.86
8.	Cu *bis*-methoxypropyl-B (demihydrate)	2.125	1100	204	1304	1.79

[B denotes biguanide sulphate].

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DISTRIBUTION OF ELECTROLYTES ACROSS A SEMIPERMEABLE MEMBRANE IN THE PRESENCE OF COLLOIDAL SILICA

By M. J. Patani and P. J. Patani

The hydration in the case of silica sol has been found out by studying the distribution of chloride added as a reference substance across a semipermeable membrane. Neglecting the membrane equilibrium effect, the value of hydration is 33.3 moles of water per g. of colloid. The charge on the micelles in terms of ammonium ion per g. of silica has also been calculated, and it comes out to be 0.14.

When silica sol containing sodium chloride as a reference substance is kept in a collodion bag and allowed to come to an equilibrium with the diffusate outside the bag, there is an unequal distribution of sodium chloride across a semipermeable membrane, which is attributed to the following effects: The amount of chloride per unit volume is less within the bag than that outside due to (*a*) establishment of the Donnan membrane equilibrium effect (Donnan, London Physiological Society, December, 1910; *Z. Elektrochem.*, 1911, **17**, 572; *Chem. Rev.*, 1924, **1**, 73) and (*b*) the volume occupied by the colloidal micelles, *i.e.*, the volume of the colloidal silica plus water attached to it (which does not function as a solvent for the chloride). On the other hand, the adsorption of ammonium silicate or the ammonium hydroxide, the stabilising electrolytes, by the micelles will lead to the increase of ammonium ion inside the bag as compared to that outside the bag. In the case of negatively charged silica sol, the chloride ions are not likely to be adsorbed (Bolam and Trivedi, *Trans. Faraday Soc.*, 1942, **38**, 140; Trivedi and Patani, *Proc. Ind. Acad. Sci.*, 1953, **37A**, 33). So far as we are aware, no direct attempt has been made to measure the extent of hydration in the case of these sols on similar lines.

Experimental

In the present investigation the silica sol was prepared by adding slowly concentrated sodium silicate solution to hydrochloric acid solution in required proportion and subjecting the mixture to cold continuous dialysis until it was turned to gel. The gel so formed was peptised by a small quantity of ammonia. The excess of ammonia was removed by heating the sol on a water-bath.

Silica content of the sol was estimated directly by evaporating an aliquot portion of the sol to dryness in a previously weighed crucible. Chloride was estimated by Volhard's method (Vogel, "A Text-Book of Quantitative Inorganic Analysis", 1955, p. 473). An aliquot portion of the sol was coagulated by sodium sulphate. The filtrate with its washings was employed for determination of the chloride content. To determine ammonium ion, an aliquot portion of the sol was coagulated, filtered, washed and the filtrate was treated with an excess of standard NaOH solution. The solution was boiled till free of ammonia, cooled and the excess of NaOH added was titrated against standard HCl (Vogel, *ibid.*, p. 305).

A partially dialysed sol, mixed with sodium chloride (far below C.V.) was kept in collodion bags, suspended in water. After attainment of equilibrium the sol inside (I) and very dilute sol (E) outside the bags were analysed for different constituents. The results of membrane equilibrium experiments are shown in Table I.

TABLE I

Expt.	Conc. of silica (g./litre).		Conc. of chloride (m.e./litre).		*D.*	S.H.V.
	(I).	(E).	(I).	(E).		
1	44.7	4.9	25 4	46.4	0.08794	25 01
2	43.5	5.0	25.4	46.4	0.08507	25.86
3	45.5	5.9	29.5	4 .5	0 10100	21.77
4	46.7	5.3	29.0	48.0	0.10460	21.04
5	46 3	3.6	26.5	48 5	0 09412	23.37
6	46.1	6.4	28.5	49 5	0.09358	23.51
7	48.9	4.1	29.0	49.5	0.10510	20.33
8	46.1	3.9	28.0	49.5	0.09705	22.64
9	47.0	4 1	28.0	48.5	0.10150	21.68
10	41.0	4.9	27.0	47 0	0.08484	25.93
11	45.0	3.9	28.5	47.0	0.10440	21.07
					Mean 0.097	22.90

TABLE II

Expt.	Conc. of silica (g./litre).	Conc. of NH_4^+ (m.e./litre).		Free NH_4^+ calc. for "1"	Fixed NH_4^+.	NH_4^+ ion per g. of colloid.
	(I—E).	(I).	(E)	(in m. e. per litre).		
1	39.8	8.8	4.0	2.19	6.61	0.16
2	38.5	9.0	4.0	2.19	6.81	0.17
3	39.6	8.4	5.8	3.53	4.87	0.12
4	41.4	8.6	6.0	3 62	4.98	0.12
5	42.7	9.2	5.4	2.95	6.25	0.14
6	39.7	8.6	4.8	2.76	5.84	0.15
7	44.8	10.4	6.6	3.87	6.53	0.14
8	42.2	8 8	5.4	3.06	5.74	0.13
9	42.9	8.0	4 4	2.54	5.46	0.13
10	36.1	9.0	4.6	2.64	6.36	0.17
11	41.1	8.6	5.0	3.03	5.57	0.13
						Mean 0.14

DISCUSSION

From Tables I and II the concentration of chloride (E) outside the bag appears to be greater than (I) inside the bag. The reverse is the case with NH_4^+ ions. In silica sol, the concentration of silica outside the bag is about 10% of the concen.ration inside the bag. Since ammonium ion is the gegenion, it may exist both in the fixed as well as in the free condition. Assuming that chloride is unadsorbed (sodium chloride added as a reference substance), the distribution of chloride across the membrane will be in the same ratio as that of free NH_4^+ ions. Hence, knowing

the concentration of chloride on both sides of the membrane, and of free ammonium ion outside the membrane, the concentration of free NH^4 ions inside the membrane, and hence of the fixed ammonium ion inside the membrane may easily be calculated. This value in all the cases is less than the concentration of NH_4^+ ions inside the bag found experimentally (Table II). The difference between the two values will be the concentration of fixed ammonium ion. The concentration of fixed ammonium ion per g. of silica is 0.14 m.e. approximately.

Unequal distribution of chloride across a semipermeable membrane in the case of silica sol may allow us to calculate either (*a*) the hydration or (*b*) the membrane equilibrium effect, provided that the other is known. Thus, if the membrane equilibrium effect was estimated independently, the hydration effect could have been calculated. A suitable method to estimate membrane equilibrium effect could not be devised; however, if the concentration of the diffusible ions is much greater than that of the non-diffusible ions, the membrane equilibrium effect will be of lesser importance as compared to the hydration effect (McBain, "Colloid Science", 1950, p. 214).

In the present case, the concentration of diffusible ions is several times that of the non-diffusible ions. Besides, only a fraction of the latter may contribute to the membrane equilibrium effect (Bjerrum, *Z. physikal. Chem.*, 1924, **110**, 656). If the membrane equilibrium effect is neglected, the difference in the chloride concentration outside and inside the membrane may be attributed to the hydration of the micelles *i.e.*, a part of the solvent is immobilised in the colloidal particles. From this the apparent density, *D* and the specific hydrodynamic volume, S.H.V., can be calculated as shown before (Trivedi and Patani, *Proc. Ind. Acad. Sci.*, 1954, **40A**, 119). Taking the average value of S.H.V. as 23 (Table I) and the density of SiO_2 as 2.2 ("Chemical Engineer's Hand Book", 1911, p. 434), there will be 22.0 g. of non-solvent water to 2.2 g. of silica, *i.e.* $(22/18) \times (60/2.2) = 33.3$ moles of water per mole of silica. The term hydration may include several types of hydration (Jirgensons and Straumanis, "Colloid Chemistry", 1954, p. 326). There may be tightly bound water due to hydrogen bonds. The conclusion of Mooney (*J. Colloid Sci.*, 1951, **6**, 162), that there may be only one or two molecules of water per molecule of silica, probably refers to this type. On the other hand, loosely adsorbed water (by dipole attraction and cohesion) will depend upon the nature of particles in the sol. While the chemically bound water is dependent only on the chemical nature of the parent substance (SiO_2), the physically bound water contributes largely to the physical properties of the sol, like viscosity etc. In addition, there may be trapped water in gels. All these three types of water are included in the term hydration. In order to determine the effect of hydration on the stability of the sols, it will be necessary to determine the extent of different types of hydration.

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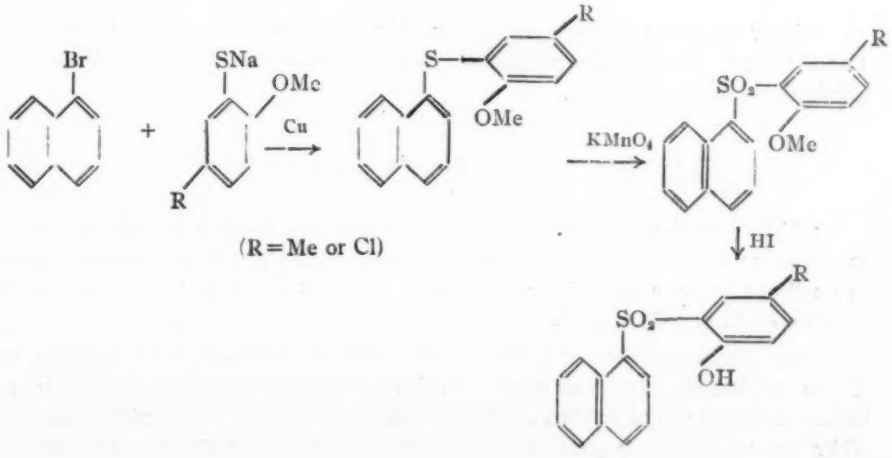
FRIES REARRANGEMENT OF ARYL NAPHTHALENESULPHONATES AND NAPHTHYL ARENESULPHONATES

By V. Balasubramanian and V. Baliah

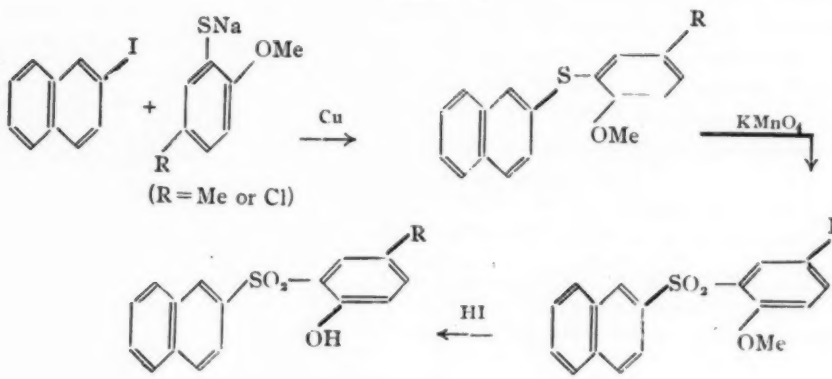
The rearrangements of four aryl naphthalenesulphonates and three naphthyl arenesulphonates under the influence of anhydrous aluminium chloride are described. The structures of the resulting hydroxysulphones have been established by synthesising them unambiguously.

The work reported in this paper is in continuation of our earlier publications on the Fries rearrangement of aryl sulphonates (Aleykutty and Baliah, this *Journal*, 1954, **31**, 513; 1955, **32**, 773; 1956, **33**, 189; Baliah and Mrs. Aleykutty Mathew, *ibid.*, 1957, **34**, 581; Baliah and Miss Uma, *Rec. trav. chim.*, 1958, **77**, 667). The rearrangement of *p*-tolyl α-naphthalenesulphonate, *p*-chlorophenyl α-naphthalenesulphonate, *p*-tolyl β-naphthalenesulphonate, *p*-chlorophenyl β-naphthalenesulphonate, β-naphthyl benzenesulphonate, β-naphthyl *p*-toluenesulphonate and β-naphthyl *o*-toluenesulphonate has been studied in the present investigation. The sulphonates underwent rearrangement when heated to 140-60° for 2 to 4 hours. Though a considerable amount of the sulphonate became charred, a small amount of alkali-soluble product could be isolated in all the cases. The product in each case was found to be the *o*-hydroxysulphone, though in some of the cases studied, formation of the *para* isomer was also possible. The identity of the sulphones was established by synthesising them unambiguously according to schemes I, II and III.

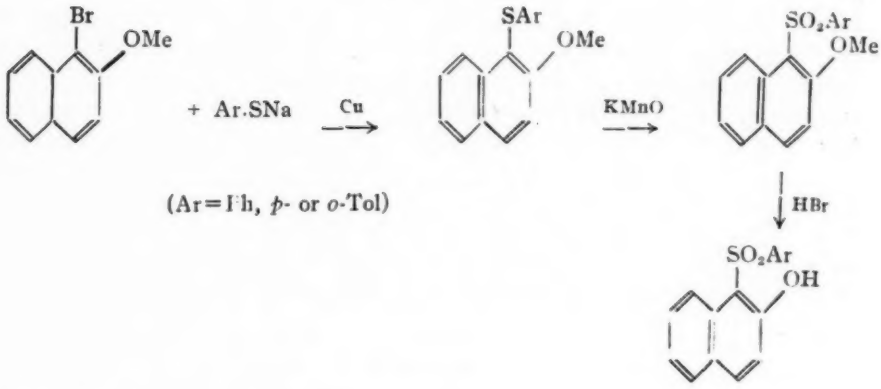
Scheme I



SCHEME II



SCHEME III



Rittler (D.R.P. 532, 403/1930; *Chem. Abs.*, 1932, **26**, 153) reported the isomerisation of phenyl β-naphthalenesulphonate, but the structure of the resulting hydroxysulphone was not established.

EXPERIMENTAL

p-*Tolyl* α-*naphthalenesulphonate* was prepared by treating a solution of *p*-cresol in ethanolic potash with α-naphthalenesulphonyl chloride. The sulphonate crystallised as small needles from ethanol, m.p. 79-80°. (Found: C, 68 42; H, 4.53. $C_{17}H_{14}O_3S$ requires C, 68.42; H, 4.73%).

Fries Rearrangement of p-*Tolyl* α-*Naphthalenesulphonate.*—An intimate mixture of the sulphonate (9 g.) and finely divided anhydrous aluminium chloride (12 g.) was heated gradually to 140-50° in an oil-bath and kept at that temperature for 2 hours. After cooling, the brown reaction mixture was decomposed with ice and HCl (conc.).

TABLE I

Naphthyl and aryl sulphonates.

No.	Sulphonate.	M.P.	Cryst. form.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	*p*-Tolyl β-naphthalene-	99-100°	Colorless needles	$C_{17}H_{14}O_3S$	68.32	68.42	4.62	4.73
2.	*p*-Chlorophenyl α-naphthalene-	97-98°	Needles	$C_{16}H_{11}O_3ClS$	60.42	60.27	3.62	3.48
3.	*p*-Chlorophenyl β-naphthalene-	73-74°	,,	$C_{16}H_{11}O_3ClS$	60.27	60.27	3.78	3.48
4.	β-Naphthyl benzene-*	105-107°	,,	$C_{16}H_{12}O_3S$	...	...	...	...
5.	β-Naphthyl *p*-toluene-**	125-26°	Lustrous leaflets	$C_{17}H_{14}O_3S$	...	...	...	...
6.	β-Naphthyl *o*-toluene-	91-92°	Needles	$C_{17}H_{14}O_3S$	68.98	68 42	4.70	4.73

* Ritter (D R. P. 532, 403/1930; *Chem. Zentrl.*, 1931, II, 3264) reports the same m.p.
** Reverdin and Crepieux (*Ber.*, 1901, **34**, 2999) report the same m p.

TABLE II

Hydroxysulphones obtained from the Fries reaction.

*Sulphonate isomerised.	Sulphone.	Yield.	M.P.	Crystalline form.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	β-Naphthyl-2-hydroxy-5-methylphenyl-	2%	159-60°	Plates	$C_{17}H_{14}O_3S$	68.13	68.42	4.77	4 73
2.	α-Naphthyl-2-hydroxy-5-chlorophenyl-	2	157-58°	Needles	$C_{16}H_{11}O_3ClS$	60.77	60.27	3.40	3.48
3.	β-Naphthyl-2-hydroxy-5-chlorophenyl-	3	125-26°	,,	$C_{16}H_{11}O_3ClS$	60.94	60.27	3.45	3.48
4.	2-Hydroxy-1-naphthylphenyl-	12	125-26°	Leaflets	$C_{16}H_{12}O_3S$	67.10	67.62	4.18	4.26
5.	**2-Hydroxy-1-naphthyl-*p*-tolyl-	2	130-31°	Needles	$C_{17}H_{14}O_3S$	68.68	68 42	5.24	4.73
6.	2-Hydroxy-1-naphthyl-*o*-tolyl-	10	158-59°	,,	$C_{17}H_{14}O_3S$	68.69	68.42	5.43	4.73

* The number refers to the corresponding sulphonates in Table I.
** Bruce and Thomson (*J. Chem. Soc.*, 1954, 1428) prepared it by the oxidation of 2-hydroxynaphthyl *p*-tolyl sulphide.

TABLE III

Sulphides and sulphones obtained by synthesis.

*Compounds.	Yield.	M.P.	Cryst. from.	Formula.	% Carbon.		% Hydrogen.	
					Found.	Calc.	Found.	Calc.
β-Naphthyl-2-methoxy-5-methylphenyl-S_1	50%	232-34°/10 mm.	Colorless oil	$C_{18}H_{16}OS$	76.66	77.13	5.79	5.73
β-Naphthyl-2-methoxy-5-methylphenyl-S	70	142-43°	...	$C_{18}H_{16}O_3S$	69.20	69.20	5.48	5.16
β-Naphthyl-2-hydroxy-5-methylphenyl S	40	159-60°	Plates	$C_{17}H_{14}O_3S$	68.28	68.42	4.70	4.73
α-Naphthyl-2-methoxy-5-chlorophenyl-S_1	60	101-12°	Small needles	$C_{17}H_{13}OClS$	67.76	67.86	4.36	4.36
α-Naphthyl-2-methoxy-5-chlorophenyl-S	80	194-95°	,,	$C_{17}H_{13}O_3ClS$	60.91	61.34	4.17	3.94
α-Naphthyl-2-hydroxy-5-chlorophenyl-S	50	156-57°	,,	$C_{16}H_{11}O_3ClS$	60.49	60.27	3.37	3.48
β-Naphthyl-2-methoxy-5-chlorophenyl-S_1	70	79-80°	Plates	$C_{17}H_{13}OClS$	67.44	67.80	4.94	4.36
β-Naphthyl-2-methoxy-5-chlorophenyl-S	100	170-72°	Needles	$C_{17}H_{13}O_3ClS$	61.37	61.34	4.15	3.94
β-Naphthyl-2-hydroxy-5-chlorophenyl-S	40	124-25°	...	$C_{16}H_{11}O_3ClS$	60.12	60.27	4.12	3.48
2-Methoxy-1-naphthylphenyl-S_1	70	79-80°	...	$C_{17}H_{14}OS$	76.26	76.63	5.59	5.30
2-Methoxy-1-naphthylphenyl-S	100	93-94°	Needles	$C_{17}H_{14}O_3S$	68.77	68.42	5.43	4.73
2-Hydroxy-1-naphthylphenyl-S	30	126-27°	Flat needles	$C_{16}H_{12}O_3S$	67.56	67.62	4.31	4.26
2-Methoxy-1-naphthyl-*p*-tolyl-S_1	60	123-24°	Rectangular prisms	$C_{18}H_{16}OS$	77.21	77.13	5.72	5.73
2-Methoxy-1-naphthyl-*p*-tolyl-S	50	137-38°	...	$C_{18}H_{16}O_3S$	69.53	69.20	5.37	5.16
2-Hydroxy-1-naphthyl-*p*-tolyl-S	50	129-30°	Needles	$C_{17}H_{14}O_3S$	68.25	68.42	4.50	4.73
2-Methoxy-1-naphthyl-*o*-tolyl-S_1	60	129-30°	Plates	$C_{18}H_{16}OS$	77.16	77.13	5.67	5.73
2-Methoxy-1-naphthyl-*o*-tolyl-S	70	165-66°	Needles	$C_{18}H_{16}O_3S$	69.44	69.20	4.96	5.16
2-Hydroxy-1-naphthyl-*o*-tolyl-S	40	158-59°	...	$C_{17}H_{14}O_3S$	68.29	68.42	4.35	4.73

* S and S_1 indicate respectively sulphone and sulphide.

The brittle solid was filtered and dried. The dry product was repeatedly extracted with ether. The ether extract was then extracted with successive portions of 10% NaOH till no more alkali-soluble product was present in the ether layer. The combined alkali extract was acidified. The pasty mass that separated solidified slowly. The yield was poor (5%). After repeated crystallisations from ethanol, almost colorless plates melting at 161-62° were obtained. There was no depression in melting point when mixed with a synthetic specimen of α-naphthyl-2-hydroxy-5-methylphenylsulphone (Found : C, 68.21 ; H, 4.75. Calc. for $C_{17}H_{14}O_3S$: C, 68.42 ; H, 4.73%).

α-Naphthyl-2-methoxy-5-methylphenyl Sulphide.—To a solution of sodium ethoxide (0.8 g. of sodium in 10 c.c. of absolute ethanol), 2-methoxy-5-methylthiophenol (5.2 g.) was added and the mixture evaporated to dryness The resulting sodium salt was mixed with α-bromonaphthalene (6.9 g) and copper powder (1 g.) and heated at 230-40° for 4 hours. After cooling, the dark brown mass was transferred to a flask and steam-distilled after the addition of H_2SO_4 (1 : 1 ; 25 c.c.) and zinc dust (5 g.). The residue was repeatedly extracted with ethanol. On evaporating off the solvent, the sulphide was obtained as a viscous mass that solidified slowly ; yield 7 g. (75%). It was crystallised from ethanol as small needles, m.p. 81-82°. (Found : C, 76.99 ; H, 5.64. $C_{18}H_{16}OS$ requires C, 77.13 ; H, 5.73%).

α-Naphthyl-2-methoxy-5-methylphenylsulphone.—A solution of the foregoing sulphide (3 g.) in hot glacial acetic acid was treated with an excess of 5% $KMnO_4$ solution and kept aside for 20 minutes. The solution was then decolorised with sodium sulphite. The sulphone that separated (2.8 g., 90%) was crystallised from dilute ethanol as colorless needles, m.p. 175°. (Found : C, 69.56 ; H, 5.28. $C_{18}H_{16}O_3S$ requires C, 69.20 ; H, 5.16%).

α-Naphthyl-2-hydroxy-5-methylphenylsulphone.—A mixture of the above sulphone (1 g.) and HI (*d* 1.7, 10 c.c.) was heated at 170-80° for 4 hours. On pouring the product into water, it solidified. The solid was filtered off, washed with water and digested with a 10% NaOH solution. On acidification of the alkali extract, the hydroxysulphone was obtained in 60% yield. Recrystallisation from aqueous ethanol furnished colorless needles, m.p. 160°. (Found : C, 68.87 ; H, 4.76. $C_{17}H_{14}O_3S$ requires C, 68.42 ; H, 4.73%).

The relevant data regarding (1) the other sulphonates isomerised, (2) the products obtained and (3) the compounds synthesised to establish their identity unequivocally are recorded in Tables I, II and III respectively. The experimental procedure adopted for their preparation was essentially the same as described for the foregoing series of compounds.

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THE INFLUENCE OF ULTRASONIC WAVES ON GOLD HYDROSOL

By Satya Prakash and Ashim Kumar Ghosh

Gold hydrosol, prepared by the reduction of chloroauric acid with formaldehyde, was exposed to ultrasonic waves of frequency 1 Mc/s and power 225 watts The ultrasonic waves have been found to cause the coagulation of the sol in much the same way as with electrolytes. The coagulation is accompanied by change of colour. The bright red sol flocculates forming secondary aggregates, the colour changing through violet, blue, then slight clouding, ultimately resulting in the precipitation of fine black particles of gold.

In previous communications (*Kolloid Z.*, 1957, **151**, 72 ; 1958, **158**, 33 ; **160**, 33) we reported our investigations on several colloids. In this paper the results on the gold hydrosol are being reproduced. The ultrasonic waves were obtained from Mullard's high frequency ultrasonic generator, type E-7562.

Experimental

The gold sol was prepared by the reduction of chloroauric acid with formaldehyde. To distilled water (500 c.c.) 0.5% chloroauric acid solution (5 c.c.) was added. The solution was made alkaline by carefully adding $N/10$-KOH solution, brought to boiling and then 0.3% formaldehyde solution (3 c.c.) was added slowly with constant stirring. Heating was continued till deep red-coloured sol was obtained. It was boiled for a few minutes more to expel the excess of formaldehyde. The sol was dialysed for a week. The concentration of the sol was 0.1053 g. Au/litre.

A constant volume of the sol was exposed each time to ultrasonic waves at a frequency of 1 Mc/s and power 225 watts per cm^2. Such adjustments were made as to provide a very good fountain accompanied with a dense fog. Under these conditions the cavitation phenomenon exerted its maximum influence. The complete experimental arrangement has been described previously (*loc. cit.*, p. 33).

Two sets of experiments were carried out each time, one with the dialysed sol and the other with undialysed one. The changes in H^+-ion concentration and electrical conductivity after the exposures are recorded in Table II. The change in the colour of the sols was followed with a spectrophotometer for wave-lengths 400-700 mμ. The results of the dialysed sol are shown graphically in Fig. 1, and that for the undialysed sol in Table III. The undialysed sol did not show any change in colour and nor did it become unstable. The change in colour from red to violet was quite prominent in the case of a dialysed sol. A visual chart is shown in Table I. The sol precipitated out on long exposures. If a short exposure was given, the coagulation took place simply on keeping overnight.

Table I

Exposure (mins.) ...	0	30	60	90
Colour (visual) ...	Bright red	Red	Violet	Dark violet

FIG. 1

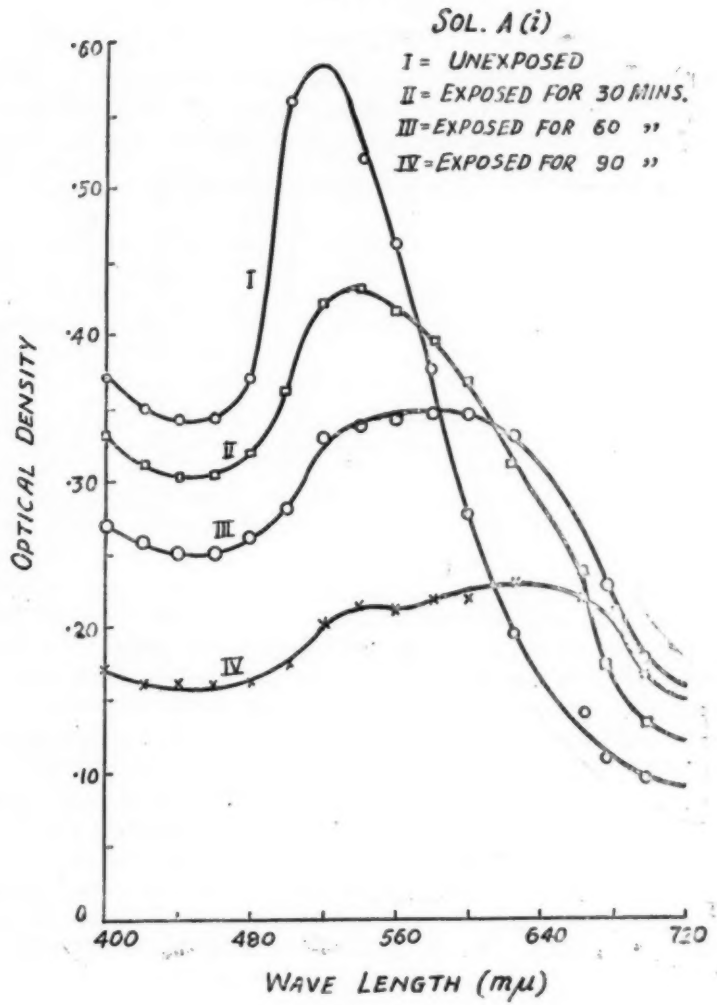

TABLE II

Temp. = 25°.

Exposure.	pH		Sp. conduc. × 10^4	
	Dialysed.	Undialysed.	Dialysed.	Undialysed.
0 min.	7.1	10.2	0.34 mhos	15.93 mhos
30	4.3	10.1	0.85	16.55
60	3.8	10.0	1.71	17.16
90	3.4	9.9	2.14	17.61
150		9.7		17.91
210		9.4		18.02

TABLE III

Undialysed sol.

Wave-length.	Exposure.			
	0 min.	60 mins.	150 mins.	210 mins.
	Optical density.			
400 mμ	0.465	0.465	0 460	0.460
420	0.450	0.450	0 450	0.450
440	0.440	0 445	0.445	0.445
460	0.450	0.455	0.460	0.455
480	0.490	0.490	0.495	0.490
500	0.600	0 600	0.605	0.605
520	0.710	0.710	0.710	0.715
540	0.690	0.690	0.690	0.690
560	0.550	0.545	0.550	0.545
580	0.390	0.385	0.380	0.385
600	0.280	0.280	0.280	0 280
625	0.195	0.190	0.190	0.190
650	0.150	0.125	0.125	0.125
700	0.125	0.120	0.120	0.120

DISCUSSION

The irradiation of gold sols with ultrasonic waves causes the coagulation of the sols in much the same way as with electrolytes However, the undialysed sols, prepared by the method described, show a remarkable stability. They do neither show a change in colour, nor they are coagulated. This is probably due to the excess of the stabilising hydroxyl ions present in the sol as impurity. The addition of electrolytes to the unprotected bright red sols causes flocculation, forming secondary aggregates and this is simultaneously accompanied by a colour change to violet, blue and then slight clouding, and ultimately resulting in the precipitation of fine black particles of gold. It would be seen from the results recorded in the foregoing tables that such changes are observed with a gold sol when it is exposed to ultrasonic waves We find also that with exposure, the plot of the optical density against wave-length becomes more and more flat. As agglomeration of particles increases, the curves become irregular and do not possess the original characteristics of the unexposed sol.

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CRITICAL STUDY OF THE STANDARD ELECTRODE POTENTIAL (E_o) DEVELOPED IN PERMANGANATE—SULPHURIC ACID AND PERMANGANATE—HYDROCHLORIC ACID SYSTEMS

By Tara Chandra Gupta and Abani K. Bhattacharya

Redox titrations with permanganate solution in presence of HCl do not provide accurate values and, hence, sulphuric acid is recommended. An effort has been made to study the standard redox potential of $KMnO_4$ in presence of H_2SO_4 and HCl under varying concentrations of acids at different intervals of time. The values of redox potential in presence of H_2SO_4 afford a constant value of E_o which corresponds to the equillibrium,

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O,$$

while the redox values in presence of HCl show wider variations with increasing concentration of the acid. This is responsible for the inaccurate results obtained in the titrations carried out by permanganate in the presence of HCl. The addition of $MnSO_4$ or $MnSO_4 + H_3PO_4$ to the $KMnO_4$-HCl system stabilises the value of E_o within the concentrations of HCl used. Hence, the Reinhardt-Zimmermann reagent is effective in controlling the errors of titration of Fe^{2+} against $KMnO_4$ in HCl system.

Although redox titrations against $KMnO_4$ in the presence of HCl are not suitable, this method has been adopted in the analysis of iron ores in industries by employing the preventive solution (Reinhardt-Zimmermann reagent). The importance of the use of HCl lies in the fact that the ores are more easily dissolved in it than in sulphuric acid. By adding the preventive solution, which is a mixture of sulphuric acid, phosphoric acid and manganous sulphate (*Ber.*, 1881, **14**, 779; *Stahl u. Eisen*, 1889, **4**, 704; *Chem. Z.*, 1889, **13**, 323; *Z. anal. Chem.*, 1897, **37**, 794) oxidation of chloride ion seems to be arrested to such an extent that fairly satisfactory results are obtained for industrial purposes. Krutwing and Cocheteux (*Ber*, 1883, **16**, 1534) observed that the inaccuracy due to the presence of hydrochloric acid could also be controlled by adding zinc and sulphuric acid in excess.

Recently Suryanarayana and Somasundaram (this *Journal*, 1955, **32**, 45) claimed that addition of sodium acetate or of borax served as an equally strong preventive mixture as the Zimmermann-Reinhardt reagent in the titration of ferrous salts in the presence of 20 c.c. of 5*N*-HCl in place of H_2SO_4. From their observations it appears that the preventive action is due to the control of H^+-ion concentration, but the Zimmermann-Reinhardt reagent has no reason to play any such role.

The titration of potassium permanganate in presence of H_2SO_4 and HCl does not seem to have received adequate attention from the aspect of the E_o values in both the systems in a comparative sense. Thus, it becomes imperative to investigate the problem further in order to explain the mechanism of the reaction. Haehnel (*Z. Elektrochem.*, 1910, **15**, 834) and Brown and Tefft (*J. Amer. Chem. Soc.*, 1926, **48**, 1128) observed that the redox potential of the $KMnO_4$—HCl system suffered

variations due to the formation of manganic chloride and changes of H^+-ion concentration.

Although according to Latimer ("Oxidation Potential", 2nd ed., p. 240) permanganate is unstable with respect to its reduction by water and at a high concentration of the acid, we have observed that the electrode potential varies but little after some manganese dioxide has been precipitated. From this it may be assumed that the system reaches fairly a stage of equilibrium after a certain time to warrant the comparative values of E_o in the $KMnO_4$—H_2SO_4 and $KMnO_4$—HCl systems. The interval of time required for this stage is, however, specific with the system. This serves as the only means for computations with sufficient accuracy in the case of half reactions that establish their equilibrium very slowly, where more than a week is required to obtain a steady redox potential, as had been observed in another similar system containing dichromate and chromic ions (Rieman, Neuss and Naiman, "Quantitative Chemical Analysis", 3rd ed., 1951, p. 202).

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O.$$

The curves showing the changes in the redox potentials of the systems:

$$MnO^-_4 \rightleftharpoons Mn^{2+} \text{ and } Cr_2O_7^{2-} \rightleftharpoons 2Cr^{3+}$$

bear out this fact fairly well (Rieman *et al.*, *ibid.*, p. 470). Gerbachev and Shpitalskiff (*J. Gen. Chem. U.S.S.R.*, 1940, **10**, 1961) observe that in the variations of oxidation-reduction potential of Mn^{3+}/Mn^{2+}, which depends upon the concentration of H_2SO_4, a stable equilibrium is produced with a small concentration of Mn^{4+} in the H_2SO_4 solution. Hugus and Latimer (*J. Electrochem. Soc.*, 1951, **98**, 296) calculated the value of heat of reaction of the system:

$$MnO^-_4 + \tfrac{5}{2}H_2 + 3H^+ = Mn^{2+} + 4H_2O$$

and observed that the free energy F° corresponded to a value of $E_o = -1.51$ volts. The redox potential in this $KMnO_4$—H_2SO_4 system agrees with the value, showing that this system attains a fairly stable equilibrium state. In $KMnO_4$—HCl system the values were, however, variable with time and the concentration of the acid.

With a view to ascertaining the role of manganous sulphate and phosphoric acid in the $KMnO_4$—HCl system, we have determined the values of E_o to explain the mechanism of the redox titrations in the presence of the Reinhardt-Zimmermann reagent. The results are recorded in the present communication.

EXPERIMENTAL

Standard solutions of $KMnO_4$, HCl, H_2SO_4, H_3PO_4 and $MnSO_4.H_2O$, all of A.R. quality, were prepared. The proportions of mixing these components with 10 c.c. of $KMnO_4$ in the total volume of 20 c.c. are recorded in the tables.

$KMnO_4$—H_2SO_4 *System.*—It was observed that H_2SO_4 reacted with $KMnO_4$ very slowly as a very small quantity of MnO_2 was precipitated in 12 days. The E.M.F. at the point of equilibrium was determined against a saturated calomel electrode and the values of the redox potential were calculated by the following formulae:

$$E = E_0 + \frac{RT}{5f} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]} \quad \ldots \quad \ldots \quad (1)$$

$$E = E_0 + \frac{RT}{3f} \log \frac{[MnO_4^-][H^+]^4}{[MnO_2]} \quad \ldots \quad \ldots \quad (2)$$

which reduces to

$$E = E_0 + \frac{RT}{3f} \log [MnO_4^-][H^+]^4,$$

assuming that the activity of MnO_2 is unity.

$KMnO_4$ – HCl *System.*—In this system the reaction with $KMnO_4$ afforded a small amount of the precipitate of MnO_2 much more quickly, depending on the amount of HCl added. Hence, the E.M.F. was observed at shorter intervals than with H_2SO_4 (vide Table II), 24 hours being the longest time of our observations. Before measuring the electrode potential, E, the excess of the liberated Cl_2 was expelled with a filter pump so that the system might contain only as much chlorine as would remain in the solution to maintain the equilibrium, $Cl_2 + 2e \rightleftharpoons 2Cl^-$. The values of the redox potentials were then calculated by the formulae :

$$E = E_0 + \frac{RT}{3f} \log \frac{[MnO_4^-][H^+]^8[Cl^-]^2}{[Mn^{2+}][Cl_2]} \quad \ldots \quad (3)$$

(according to the reaction $MnO_4^- + 2Cl^- + 8H^+ + 3e \rightleftharpoons Mn^{2+} + 4H_2O + Cl_2$) and

$$E = E_0 + \frac{RT}{f} \log \frac{[MnO_4^-][H^+]^4[Cl^-]^2}{[MnO_2][Cl_2]} \quad \ldots \quad (4)$$

(according to the reaction $MnO_4^- + 2Cl^- + 4H^+ + e \rightleftharpoons MnO_2 + Cl_2 + 2H_2O$), which reduces to

$$E = E_0 + \frac{RT}{f} \log \frac{[MnO_4^-][H^+]^4[Cl^-]^2}{[Cl_2]},$$

assuming the activity of MnO_2 as unity.

Estimations of MnO_4^-, MnO_2 *and* Mn^{2+}.—The initial concentration (A) of $KMnO_4$ and the concentration (B) of the residual permanganate were determined iodometrically ; the precipitated MnO_2 was removed by filtering through a sintered glass crucible and the concentration of the precipitated MnO_2 (C) was estimated by oxalic acid• treatment. Therefore (A) – (B) = (C) + (D), where D is the concentration of Mn^{2+} ion. In this way the concentrations of MnO_4^- and Mn^{2+} ions were determined in the system to calculate E_0 from the foregoing equations.

Estimations of Cl_2 *and the* Cl^- *ions.*—The equilibrium concentrations of Cl_2 in the reacting mixtures were determined as follows.

(*a*). The total initial chloride ion concentration, $[X]$, in the HCl—$KMnO_4$ system was determtned by Volhard's method. The excess of chlorine gas was bubbled into KI solution and its concentration, $[Y]$, was determined by iodometry. After bubbling out the chlorine gas, the concentration, $[Z]$, of the total $[Cl^-]$ which remained in the system at the desired interval of time, was estimated again by Volhard's method,

after decolorising the remaining $KMnO_4$ to a colorless solution by H_2O_2 and then filtering the precipitated manganese dioxide. Then

$$[X] - [Z] = [Y] + [W],$$

where $[W]$ is the concentration of the chlorine left in solution to equilibriate with the (Cl^-) of the systsm. Thus the concentration $[W]$ of the chlorine at equilibrium $= [X] - [Y] - [Z]$.

In this way, the $[Cl^-]$ and $[Cl_2]$ were estimated and used in the calculations of the E_o values.

Estimation of (Mn^{2+}) *in the* $KMnO_4 - HCl - MnSO_4$ *and* $KMnO_4 - MnSO_4 - H_3PO_4$-HCl *Systems.*—After mixing the solutions, the precipitated MnO_2 was filtered off. The concentration of the remaining MnO_4^- in the filtrate was determined iodometrically and the concentration, $[C]$, of the (Mn^{2+}) corresponding to this amount of MnO_4^- was calculated. Since the filtrate contained an extra amount $[x]$ of Mn^{2+} ions over and above $[C]$, it was necessary to reduce the whole filtrate to Mn^{2+} salt by H_2O_2 in presence of the acid and then estimate the total concentration $[C_1]$ of Mn^{2+} ions by $KBrO_3$ (Scott, "Standard Method of Chemical Analysis", 5th ed., p. 559). Hence,

$$C_1 = C + x \text{ or } x = C_1 - C.$$

Thus the concentrations of MnO_4^- and Mn^{2+} taking part in the electrode reactions were determined.

The pH was determined by a Cambridge pH indicator, using the glass electrode.

TABLE I

Volume of $N/4$-$KMnO_4 = 10$ c.c. $\equiv 25 mM$/litre.

H_2SO_4 and H_2O varied to make the total volume 20 c.c. (E.M.F. observed after 12 days).

$4N$-H_2SO_4 used.	pH.	*MnO_4^-.	†Mn^{2+}.	E.M.F. obs. at 26°.	E_o calc. for the equations: $MnO_4^- \rightleftharpoons Mn^{2+}$.	$MnO_4^- \rightleftharpoons MnO_2$.
1 c.c.	0.9	18.5	3.4	1.17 volts	1.49 volts	1.52 volts
4	0.5	16.5	1.0	1.23	1.50	1.55
5	0.3	14.5	0.8	1.225	1.48	1.53
7	0.2	8.5	0.9	1.24	1.49	1.54
					Mean 1.49	1.53

TABLE II

Volume of $N/4$-$KMnO_4 = 10$ c.c. $\equiv 25$ mM/litre.

HCl and H_2O varied to make the total volume 20 c.c.

$4N$-HCl used.	Time.	pH.	*MnO_4^-.	†Mn^{2+}.	†Cl^-. Cl^-	*Cl_2 left in system.	E.M.F. obs. at 26°.	E_o calc. for the equations: $MnO_4^- \rightleftharpoons Mn^{2+}$.	$MnO_4^- \rightleftharpoons MnO_2$.
1 c.c.	24 hrs.	1.4	14.4	0.10	162.0	4.55	1.068 volts	1.47 volts	1.70 volts
2	1½	1.8	15.15	0.45	355.0	6.37	1.068	1.65	1.78
2	1	1.8	17.35	0.8	359.2	1.69	1.081	1.54	1.73
2	35′	1.5	19.8	0.75	377.4	1.97	1.075	1.48	1.66
3	35′	1.8	5.8	0.1	561.2	0.91	1.076	1.51	1.71

* In mM/litre.
† In mg. atom/litre.

TABLE III

Volume of $N/9.46$-$KMnO_4$ = 10 c.c. ≡ 10.57 mM/litre.
4.37N-HCl and $M/100$-$MnSO_4$. H_2O varied to make the total volume 20 c.c.

.37N-HCl.	Time.	pH.	*MnO_4^-.	‡Mn^{2+}.	‡Cl^-.	*Cl_2 left in system.	E.M.F. obs. at 33°.	E_o calc. for the equations: $MnO_4^- \rightleftharpoons Mn^{2+}$	$MnO_4^- \rightleftharpoons MnO_2$.
1 c c.	24 hrs.	1.4	3 45	...	179.4	18.85	1.028 volts	...	1.74 volts
2	1½	1.8	4.33	0.23	358.8	38.34	1.045	1.53 volts	1.83
2	1	1.8	5.03	0.64	384.0	22.10	1.044	1.50	1.80
2	35′	1.6	6.02	0.16	410.0	10.57	1.042	1.51	1.73

TABLE IV

$N/9.46$-$KMnO_4$ = 10 c.c. ≡ 10.57 mM/litre.
4.37N-HCl + $M/100$ $MnSO_4.H_2O$ + 1.08N-H_3PO_4.

Vol. of HCl+ $MnSO_4.H_2O$+ H_3PO_4+ $KMnO_4$. (in c.c.)	Time.	pH.	*MnO_4^-.	‡Mn^{2+}.	‡Cl^-.	*Cl_2 left in system.	E.M.F. obs. at 31°.	E_o calc. for the equations: $MnO^-{}_4 \rightleftharpoons Mn^{2+}$.	$MnO_4^- \rightleftharpoons MnO_2$.
2+6+2+10	35′	1.7	6 79	0.503	414.9	2.3	1.056 volts	1.50 volts	1.72 volts
2+5+3+10	35′	1.7	7.76	0.72	419.2	4.8	1.062	1.52	1.74
2+1+7+10	45′	1 5	8.73	2.80	406.0	10.0	1.061	1.50	1.71

* In mM/litre.
‡ In mg. atom/litre.

DISCUSSION

The calculated values of E_o obtained by assuming different redox-equilibria, as recorded in Tables I-IV, are full of many interesting suggestions regarding the nature of the electrode reactions between $KMnO_4$ and H_2SO_4 and $KMnO_4$ and HCl. The accuracy or inaccuracy of the redox titration with $KMnO_4$ in presence of H_2SO_4 or HCl may be presumed to be governed by the electrode potentials of the systems. The following conclusions are arrived at from the E_o values of the systems investigated by us.

(*i*). The electrode reaction equilibrium, $MnO_4^- \rightleftharpoons Mn^{2+}$, is more probable in $KMnO_4 - H_2SO_4$ system than the equilibrium $MnO_4^- \rightleftharpoons MnO_2$, as shown by the constancy of E_o values, which are suitable for all redox titrations. But in HCl–$KMnO_4$ system, which is governed by the electrode reaction,

$$MnO_4^- + 2Cl^- + 8H^+ + 3e \rightleftharpoons Mn^{2+} + Cl_2 + 4H_2O,$$

variable values of E_o have been obtained. Here also there is no support to the equilibrium $MnO_4^- \rightleftharpoons MnO_2$, the E_o values being much wider than the standard value 1.67 volts (Rieman *et al.*, *loc. cit.*, p. 472).

(*ii*). From the values of E_o in $HCl-KMnO_4$ system (Table II) it becomes evident that the degree of inaccuracy in the redox titrations will depend on the concentration of HCl added and the time of reaction.

In Table III, the values of E_o obtained in the presence of Mn^{2+} salts in $KMnO_4-HCl$ system become more steady to correspond to the equilibrium $MnO_4^- \rightleftharpoons Mn^{2+}$. Here again, there is no support for the electrode reaction $MnO_4^- \rightleftharpoons MnO_2$.

By the addition of H_3PO_4 (Table IV) to $KMnO_4-HCl-MnSO_4$ system, the values of E_o are slightly more steady, which correspond to the equilibrium, $MnO_4^- \rightleftharpoons Mn^{2+}$; but it is striking that the E_o values for the equilibrium $MnO_4^- \rightleftharpoons MnO_2$ are more establised in this system (cf. Tables III and IV).

From this we conclude that the steadiness of the E_o values contributes to the efficiency of the Reinhardt-Zimmermann reagent in the titration of Fe^{2+} salts against $KMnO_4$ in the presence of HCl. It further appears that in $KMnO_4-HCl-MnSO_4-H_3PO_4$ system, either the equilibrium $MnO_4^- \rightleftharpoons Mn^{2+}$ or $MnO_4^- \rightleftharpoons MnO_2$ may be possible.

Phosphoric acid, however, masks the yellow colour of the ferric ion by forming a complex with ferric chloride. This aspect will be elucidated in our next communication dealing with the conditions for the formation of ferric phosphate complex, and its role in the Fe^{II}-$KMnO_4$ titration in the presence of HCl.

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VAPOUR PHASE CHLORINATION OF ETHANOL UNDER SILENT ELECTRIC DISCHARGE. PART II. STUDIES IN THE MECHANISM OF REACTION*

By O. P. Malhotra

Some of the compounds obtained by vapour phase chlorination of ethanol under silent electric discharge have been subjected to indepeudent chlorination under similar conditions in order to study their role as possible intermediates in the formation of chloral and hexachloroethane, the most extensively chlorinated products. The results have been discussed and mechanism of the formation of different products has been proposed.

A qualitative study of the products of vapour phase chlorination of ethanol under silent electric discharge (Part I, this *Journal*, 1958, **35**, 99) has revealed that chloral (or its derivatives) and hexachloroethane constitute the more exhaustively chlorinated products. While it was possible that these were formed by independent processes, it was more likely, in view of their intimate relationships, that they might have been formed by a single (or more) reaction sequence (s). The same holds for other products also. In order to find out if the compounds containing a lower proportion of chlorine could be intermediates in the formation of those more exhaustively chlorinated, it was thought of interest to investigate the chlorination of some members of the former category. On account of differences in physical properties, identical conditions could not be maintained in all cases, but attempts were made to adhere to these (or the corresponding conditions) as nearly as possible.

Experimental

General arrangement of apparatus employed was the same as that used for alcohol (Malhotra, *loc. cit.*), excepting in the case of acetaldehyde. Due to the highly volatile nature of this compound the dropping funnel was maintained at 0° by fitting it in a bigger funnel filled with crushed ice. In order to protect it form radiant heat and steam from water-bath, the lower tip of the dropping funnel was fused into a long capillary tubing leading into the boiling flask.

All the liquids were added at 4 c.c./hr. and chlorine was run at 6 c.c./sec. Frequency of A.C. supply was 500 cycles/sec. Other working conditions and products obtained from different compounds are recorded in Table I.

* These studies were carried out in the Chemical Laboratories of Banaras Hindu University, Varanasi.

TABLE I

Chlorination of possible intermediates.

	Starting compound.	Operating conditions. Bath temp.	Ozonizer temp.	Applied potential.	Products obtained.
1.	Acetaldehyde	50-60°	80-90°	2.0 kv	Di- and tri-chloroacetaldehydes and hexachloroethane.
2.	Paraldehyde	150-60°	80-90°	2.5	Di- and tri-chloroacetaldehydes and hexachloroethane.
3.	Dichloroacetaldehyde	140-50°	80-90°	2.5	Trichloroacetaldehyde, hexachloroethane and dichloroacetaldehyde (unchanged).
4.	Trichloroacetaldehyde	140-50°	80-90°	2.5	Hexachloroethane and trichloroacetaldehyde (unchanged).
*5.	Monochloroacetaldehyde acetal	...	...	2.0	Di- and tri-chloroacetaldehydes, trichloroacetaldehyde alcoholate, di- & tri-chloroacetaldehyde acetals and monochloroacetaldehyde acetal (unchanged).
*6.	Dichloroacetaldehyde acetal	...	...	2.0 kv	Di- and tri-chloroacetaldehydes, trichloroacetaldehyde alcoholate, 1:2:2-trichlorodiethyl ether, trichloroacetaldehyde acetal, hexachloroethane and dichloroacetaldehyde acetal (unchanged).

*For No. 5 and 6, the boiling flask was heated directly and the water was withdrawn from the jacket which now served to protect the ozonizer from air-cooling.

DISCUSSION

The data in Part I (*loc. cit.*) and Table I above suggest the following mechanism.

First step in the vapour phase chlorination of ethanol appears to be the formation of acetaldehyde :

$$C_2H_5OH + Cl_2 \longrightarrow CH_3.CHO + 2\ HCl \quad \ldots \quad \ldots \quad (1)$$

The formation of acetaldehyde from ethanol under silent electric discharge has been observed earlier (Loeb, *Biochem. Z.*, 1909, **20**, 126). This reaction is particularly favoured by oxidative conditions (cf. Sahasrabudhe, Deshpande and Gopala Rao, *Proc. Ind. Acad. Sci.*, 1952, **36A**, 258) in the present case by the presence of chlorine which serves to remove hydrogen as HCl. Formation of acetaldehyde during liquid phase chlorination of ethanol is also well known and constitutes the first step in the mechanism proposed by Lieben (*Annalen*, 1857, **104**, 114 ; *Ber.*, 1870, **3**, 907), while Chattaway and Backeberg (*J. Chem. Soc.*, 1924, **125**, 1097) suggested its formation through ethyl hypochlorite (C_2H_5OCl), which, however, could not be detected by the present author, possibly because of its rapid decomposition into acetaldehyde.

Formation of the same products (viz. $CHCl_2CHO$, CCl_3CHO and C_2Cl_6) from both acetaldehyde and paraldehyde (Table I) indicates that either of them serves as an intermediary in the chlorination of the other or that an equilibrium is set up between the two under the influence of HCl ; the latter suggestion is supported by Primer

(*Annalen*, 1875, **179**, 21) and Chattaway and Backeberg (*loc. cit.*). The latter authors have suggested that the chlorination of acetaldehyde proceeds through its polymer to *sym.*-trichloroparaldehyde and then to monochloroacetaldehyde. In the vapour phase chlorination of acetaldehyde in the present investigation, however, some of it must have been chlorinated directly into monochloroacetaldehyde to produce HCl necessary for bringing about polymerisation.

$$\begin{array}{ccccc} C_2H_5OH & \xrightarrow{Cl_2} & CH_3CHO & \xrightarrow{Cl_2} & CH_2ClCHO \\ & & \text{HCl}\,\Downarrow\Uparrow & & \Downarrow\Uparrow\text{HCl} \\ & & (CH_3CHO)_3 & \xrightarrow{Cl_2} & (CH_2ClCHO)_3 \end{array} \qquad \ldots\ (2)$$

Reaction can now proceed in two directions, depending on whether excess of alcohol is present or not.

The occurrence of α-halo ethers in the products of chlorination of ethanol (Malhotra, *loc. cit.*) and their known formation from aldehydes (or their polymers) by reaction with alcohols and halogen acid (Natterer, *Monatsh.*, 1884, **5**, 496 ; Farren *et al.*, *J. Amer. Chem. Soc.*, 1925, **47**, 2419 ; Henze and Murchin, *ibid.*, 1931, **53**, 4077 ; Sherill and Walter, *ibid.*, 1936, **58**, 743 ; Watermann *et al.*, *Rec. trav. chim.*, 1937, **56**, 437) suggested the next steps to be as :

$$\begin{array}{ccc} CH_2ClCHO & \xrightarrow{HCl,\ C_2H_5OH} & CH_2Cl.CHCl.OC_2H_5 \\ \Downarrow\Uparrow & & \downarrow Cl_2 \\ (CH_2ClCHO)_3 & & CHCl_2.CHCl.OC_2H_5 \end{array} \qquad \ldots\ (3)$$

These two ethers then react with excess alcohol to furnish mono- and di-chloroacetaldehyde acetals respectively ; the occurrence of 1 : 2 : 2-trichlorodiethyl ether among the products obtained from dichloroacetal (Table I) suggests that this reaction may be reversible. In liquid phase this reaction is known to be reversible and catalysed by HCl (Liemu and Salomoa, *Acta Chem. Scand.*, 1947, **1**, 353). The data in Table I further suggest the conversion of monochloroacetal into di- and tri-chloro compounds by direct chlorination.

$$\begin{array}{ccc} CH_2Cl.CHCl.OC_2H_5 & \underset{HCl}{\overset{C_2H_5OH}{\rightleftharpoons}} & CH_2Cl.CH(OC_2H_5)_2 \\ \downarrow Cl_2 & & \downarrow Cl_2 \\ CHCl_2.CHCl.OC_2H_5 & \underset{HCl}{\overset{C_2H_5OH}{\rightleftharpoons}} & CHCl_2.CH(OC_2H_5)_2 \\ & & \downarrow Cl_2 \\ & & CCl_3.CH(OC_2H_5)_2 \end{array} \qquad \ldots\ (4)$$

The formation of free aldehydes during the vapour phase chlorination of acetals, now observed under silent electric discharge, suggests the dissociation of acetals into the corresponding aldehydes under electrical excitation. The aldehydes, however, possibly combined with more alcohol to form alcoholates, absence of appreciable amounts of

which might be attributed to their ready dissociation (Post, *J. Org. Chem.*, 1941, **6**, 830; Huntress, "Organic Chlorine Compounds", J. Wiley, 1948, pp. 111, 630).

Results of the experiments with acetaldehyde, paraldehyde and dichloroacetaldehyde (Table I) indicate that in the absence of ethanol, monochloroacetaldehyde obtained from acetaldehyde (*vide supra*) is directly chlorinated to di- and tri-chloroacetaldehydes (cf. Primer, *loc. cit.*; Wurtz, *Annalen*, 1857, **102**, 93; Wurtz and Voigt, *Bull. soc. chim.*, 1872, *ii*, **17**, 402).

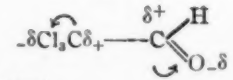
$$CH_2Cl.CHO \xrightarrow{Cl_2} CHCl_2.CHO \xrightarrow{Cl_2} CCl_3.CHO \qquad \ldots (5)$$

Absence of monochloroacetaldehyde in the products is a striking feature and is probably due to a rapid rate of reaction in the early stages, particularly in the presence of a large excess of Cl_2 and C_2H_5OH. This is in line with the results of earlier workers at higher temperatures (Guinot and Tabuteau, *Compt. rend.*, 1950, **231**, 234; Post, B.P., Oct. 1950; *Chem. Abst.* 1951, **45**, 5176).

The vapour phase chlorination of ethanol under silent electric discharge seems to proceed mostly through reactions (1), (2), (3) and (4) as is suggested by the formation of large quantities of acetals and the presence of unchanged ethanol among the products obtained earlier (Malhotra, *loc. cit.*). The possibility of the reaction proceeding simultaneously through the alternative route, reactions (1), (2) and (5), cannot, however, be summarily ruled out.

Ethyl acetate and carboxylic acids (other than acetic acid) were observed among the products of vapour phase chlorination of ethanol under silent electric discharge (Malhotra, *loc. cit.*). These seem to have been formed by polymerisation of acetaldehyde and the oxidation of chloroacetaldehydes respectively.

Hexachloroethane, apart from being the most highly chlorinated compound obtained, occurred among the products of chlorination of almost all the compounds studied and was the only product obtained from chloral. This indicated that this compound probably occurred last in the chain of reaction and was almost certainly produced by the dissociation, under electric discharge, of chloral molecules into trichloromethyl (CCl_3) and formyl (CHO) radicals. Two trichloromethyl radicals combined to afford hexachloroethane (C_2Cl_6) while formyl probably reacted with chlorine to yield such volatile products as CO, $COCl_2$, HCl, etc. A similar formation of hexachloroethane by the pyrolysis of chloral vapour in the presence of Cl_2 (or other halogens) and catalysts like $AlCl_3$ is known (Moneyrat, *Bull. soc. chim.*, 1897, *iii*, **17**, 794). Such a type of dissociation must be assumed in the formation of CCl_4, CO and HCl from chloral and chlorine at 70-90°, as observed by Alexander and Schumacher (*Z. physikal. Chem.*, 1939, **B44**, 57). This dissociation is aided by weakening of the bond between CCl_3 and CHO due to the strong electronegativities of chlorine atoms and carbonyl oxygen which act in such a manner that electron density between the two carbon atoms in



will be less than in a normal C–C bond.

It may be pointed out that exactly identical physical and chemical conditions could not be reproduced in the chlorination of all compounds (e.g. whereas a large excess of ethanol was present during its own chlorination, the studies with other compounds were, for obvious reasons, carried out in complete absence of alcohol). The above mechanism therefore represents the plausible routes through which the reaction can proced, without, necessarily, precluding the other alternative possibilities.

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BEHAVIOUR OF ELECTROLYTES IN MIXED SOLVENTS. PART IV. CONDUCTANCE OF $MgSO_4$ IN DIOXANE-WATER MIXTURES AT 35°

By P. B. Das, P. K. Das and D. Patnaik

Conductance of $MgSO_4$ in water and in dioxane-water mixtures, containing 10, 20 and 30% of dioxane, have been measured at 35°. The method of Fuoss and Kraus and that of Shedlovsky have been applied for the calculation of the equivalent conductance at zero concentration and the dissociation constant. The values obtained by the two methods are in good agreement. These values indicate that the radii of the constituent ions remain unaffected up to 20% dioxane content of the medium.

Measurements on a large scale on the conductivity of salts including that of $MgSO_4$ have been made in mixed solvents at 25°. However, such measurements at 35°, necessary for our viscosity study, are not found in the literature. The present investigation has been undertaken therefore with a view to determining the conductance of $MgSO_4$ at infinite dilution in dioxane-water mixtures of different compositions at 35°.

Experimental

Magnesium sulphate of B.D.H.-Analar quality was recrystallised from triple distilled water and was dried and stored over partially dehydrated salts. The stored sample, which was analysed for Mg^{2+} and SO_4^{2-} by standard methods (Vogel, "Text Book of Quantitative Inorganic Analysis", 1955, 2nd ed., pp. 373, 403), was found to contain seven molecules of water per molecule of magnesium sulphate. Dioxane used was of E. Merck's 'extra pure' quality. Purification of the dioxane and the preparation of the solvent were carried out as reported earlier (this *Journal*, 1957, **34**, 56).

The solution of any desired concentration was prepared by dilution from a stock solution, the exact concentration of which was determined by analysis. At all stages of the preparation and transfer of the solvent as well as of the solution, sufficient care was taken to prevent the evaporation of either of the constituent solvents. All weights and vessels used were calibrated at 35°. A Jones and Bollinger type of cell (*J. Amer. Chem. Soc.*, 1931, **53**, 411) was used. The conductance data of KCl, reported by Gunning and Gordon (*J. Chem. Phys.*, 1942, **10**, 126), were used for the determination of the cell constant which was found to be 0.0965. The viscosity measurements were carried out exactly in the same manner as described previously (*loc. cit.*). Conductance was measured with an accuracy of ± 2 in 1000. The working temperature was 35° ± 0.001°.

TABLE I

Solvent composition (conc. in equiv./litre).	Λ ohm^{-1}. 0% Dioxane. D = 74.89.	Λ ohm^{-1}. 10% Dioxane. D = 66.33.	Λ ohm^{-1}. 20% Dioxane. D = 57.73.	Λ ohm^{-1}. 30% Dioxane D = 49.19
0.004	131.60	104.50	87.90	...
0.006	125.40	97.60	76.60	46.73
0.008	120.80	91.66	67.30	40.80
0.010	117.70	86.86	63.80	32.99
0.012	109.50	85.30	58.10	31.48
0.014	108.50	81.28	57.30	30.98
0.016	106.70	77.03	56 10	28.95
0.018	104.68	75.30	52.87	28.60
0.020	102.40	75.03	50.00	27.03

TABLE II

Solvent comp. (% dioxane content).	Equiv. conduc. at infinite dilution (Λ_0) by		Dissociation constant ($K \times 10^3$) by		Radii of the ion pairs.	
	Fuoss & Kraus' method.	Shedlovsky's method.	Fuoss & Kraus' method.	Shedlovsky's method.	Bjerrum eq.	Stokes law.
0	140.84	140.84	13.20	13.09	8.40Å	6.78Å
10	113.60	113.60	6.43	6.56	8 41	7.03
20	95 24	95.24	4.24	4.02	9.12	7.07
30	64.50	64.10	2.88	3.00	11.32	9.07

DISCUSSION

The Onsager equation (*Physikal. Z.*, 1927, **28**, 277) for a completely dissociated electrolyte,

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C}$$

(where Λ, Λ_0 are the equivalent conductances at concentration C and at zero concentration ; A and B are constants), satisfactorily accounts for the change in equivalent conductance with concentration. Correct evaluation of Λ_0 can be made by extrapolating to zero concentration of the line obtained by plotting Λ against $\sqrt{C}$. However, the above methods of extrapolation have been reported by various authors (cf. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., 1950, p. 147, Reinhold, New York) to be unreliable in cases of a number of electrolytes involving incomplete dissociation or ion association. Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 475) and Shedlovsky (*J. Franklin Inst.*, 1938, **225**, 439) have suggested methods for the evaluation of Λ_0 along with the dissociation constant 'K' of the electrolyte.

For the application of these methods, our experiments provided the viscosity data (to be published later) ; the dielectric constants were taken from the data of Åkerlof and Short (*J. Amer. Chem. Soc.*, 1936, **58**, 1241) and the activity coefficients were calculated by using the Debye-Hückel limiting expression, as was used by various workers (Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488 ; Dunsmore and James, *J. Chem. Soc.*, 1951, 2925 ; Griffiths and Lawrence, *ibid.*,

1955, 1208). The functional table, recorded by Fuoss (*loc. cit.*), was used for application of their method, while that of Daggett (*J. Amer. Chem. Soc.*, 1951, **73**, 4977) was used for Shedlovsky's extrapolation method.

In Table I, the equivalent conductances of $MgSO_4$ at various concentrations in water and also in dioxane-water mixtures of different compositions have been tabulated. The values of Λ_0 and K for each solvent composition have been determined by the above two methods and are recorded in Table II. It is evident from these results that Λ_0 and K, obtained by the two methods, are in good agreement. The progressive decrease in the values of the dissociation constant with increase in dioxane content of the medium may be attributed to the lowering of the dielectric constant of the medium.

On the assumption that purely coulombic forces exist between the constituent ions, Bjerrum (Det. Kgl. Danske vide, [VII **9**, 2, 1926]) has shown that the distance 'a' between the centres of the two ions at their closest distance of approach can be calculated from the knowledge of reciprocal equilibrium constant K^{-1} of the ion pair. On the other hand, if the ions constituting the electrolytes are regarded as obeying Stokes' law, then the radius 'r' of an ion can be found from the known values of the limiting mobility for the ion. The mean diameter of the ion pair 'a' is calculated by addition of the cationic and anionic radii, thus derived, assuming, however, that the transport numbers of the ions neither change with the change in composition of the solvent nor with temperature. The radii of the ion pairs evaluated by both the methods have been recorded in Table II.

Considering the assumption made above for the activity coefficient and the transport number, the agreement between the values of the radii obtained by the two methods may be considered as satisfactory. Further, the values of the radii do not indicate much change up to 20% of dioxane content, but at 30% composition the change is noticeable. It can be stated with caution that the solvation sphere of the ions, specially that of the Mg^{2+} ion, is not very much affected until the concentration of dioxane in the solvent reaches as high as 30%.

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NATURE OF RACEMIC MODIFICATIONS OF CHLORO (*o*-, *m*- & *p*-)-, BROMO (*o*-, *m*- & *p*-)- AND NITRO (*o*-, *m*- & *p*-)-PHENYL CAMPHOR-β-SULPHONATES

By S. K. Vasistha and S. Ramagopala Sarma

The nature of racemic modifications of *o*-, *m*- and *p*-chloro-, *o*-, *m*- and *p*-bromo- and *o*-, *m*- and *p*-nitro-phenyl camphor-β-sulphonates has been studied with the aid of melting point-composition diagrams. The racemic forms of *p*-chloro-, *p*-bromo- and *m*-nitro-phenyl esters have been found to exist as solid solutions, while the racemic forms of the rest of the compounds are *dl* compounds.

The nature of the recemic forms can be decided with the help of phase rule, from a study of either the solubility or fusion curves (Roozeboom, *Ber.*, 1899, **32**, 537; *Z. physikal. Chem.*, 1899, **23**, 494; Bruni, *Gazzetta*, 1900, **30**, 35) of the opitically active and racemic substances. A third method, biochemical, is due to B. K. Singh *et al.* (*Proc. Nat. Acad Sci. India*, 1944, **14**, 171). The method based on Roozeboom's melting point-composition diagrams was employed in the present study.

Experimental

The preparation and physical properties of *o*-, *m*- and *p*-nitrophenyl camphor-β-sulphonates (*d*- and *dl*-) have been described by us in a later communication (Vasistha and Sarma, unpublished). The chloro (*o*-, *m*- and *p*-)- and bromo (*o*-, *m*- and *p*-)- phenyl esters (*d*- and *dl*-) of camphor-β-sulphonic acid were prepared in the same way as the nitrophenyl esters according to the method of Hilditch and Edmindson (*J. Chem. Soc.*, 1910, **97**, 220), substituting pyridine for sodium hydroxide solution for better yields. The esters are crystallisable from ethyl and methyl alcohols.

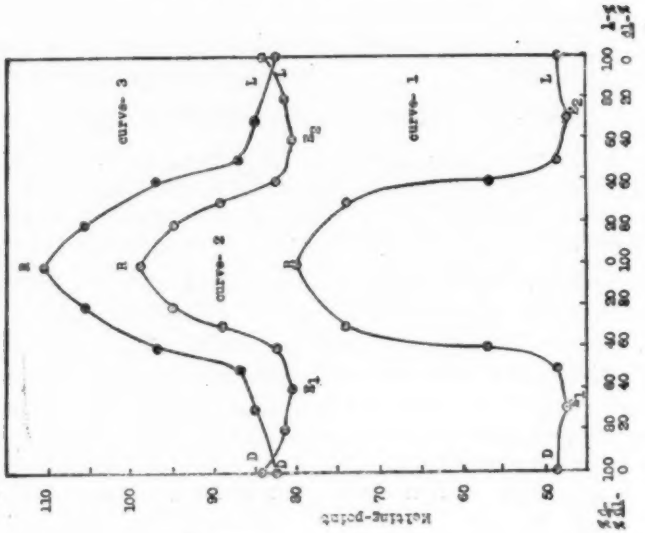
The physical properties and the results of analysis are recorded in Table I.

Table I

Esters of camphor-β-sulphonic acid.	M.P.	Crystalline form.	% Sulphur, Found.	Calc.
1. *o*-Chlorophenyl	*d*- 57.5°	Rect. plates	9.02	9.35
	dl- 100°	Thin rect. plates	9.80	,,
2. *m*-Chlorophenyl	*d*- 54.5°	Rect. plates	9.31	,,
	dl- 86.0°	,,	9.33	,,
3. *p*-Chlorophenyl	*d*- 84.5°	Prismatic needles	9.57	,,
	dl- 110°	Needles	9.40	,,
4. *o*-Bromophenyl	*d*- 84.0°	Prismatic needles	8.05	8.28
	dl- 98.5°	Thin rect. plates	8.45	,,
5. *m*-Bromophenyl	*d*- 48.5°	Rect. plates	8.35	,,
	dl- 80.0°	,,	8.23	,,
6. *p*-Bromophenyl	*d*- 82.5°	Prismatic needles	8.19	,,
	dl- 110.5°	Rect. plates	8.16	,,

N.B. All the esters are colorless. They are very soluble in chloroform and benzene, moderateyl soluble in acetone and pyridine and less so in methyl alcohol, ethyl alcohol and petroleum ether.

The melting point-composition diagrams (Figs. 1-3) were prepared as follows: The melting points of homogeneous mixtures of known proportions of *d*- and racemic forms were plotted against % composition. The melting points and the corresponding compositions are omitted for the sake of economy of space.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curve- 2
curve- 1
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E_3
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60
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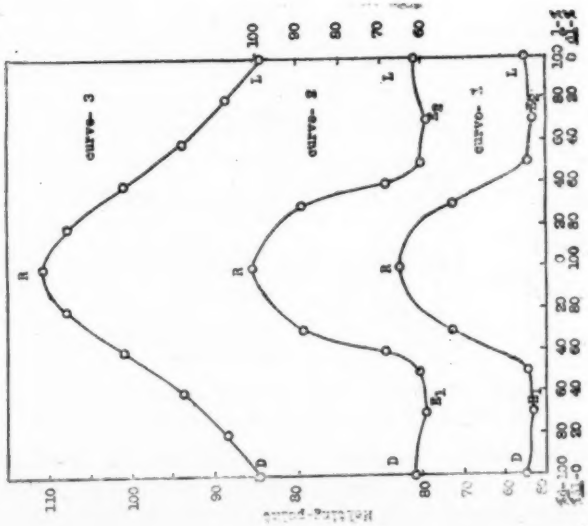
1-x
x-1

FIG. 2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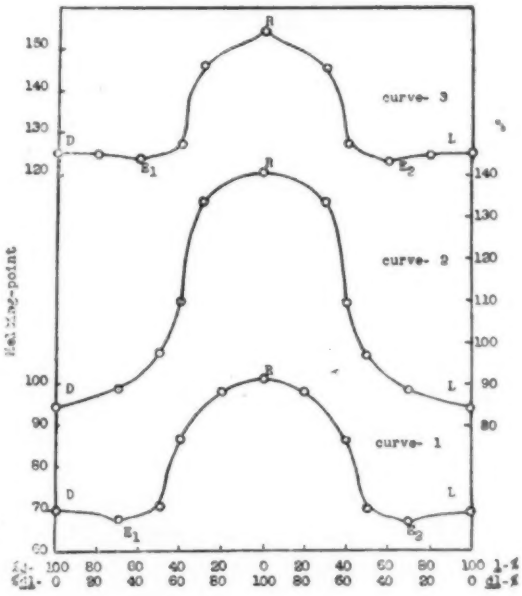
100 80 60 40 20 0 20 40 60 80 100
1-x
x-1

FIG. 1

DISCUSSION

The melting point-composition diagrams of *p*-chlorophenyl (Fig. 1, curve 3), *p*-bromophenyl (Fig. 2, curve 3) and *m*-nitrophenyl (Fig. 3, curve 2) esters of camphor-β-sulphonic acid consist of a single continuous curve, DRL, with the central maximum, R, indicating the racemic forms of these esters to be *solid solutions* of optically active and opposite isomers. Though the curves for *m*-nitro- and *p*-bromo-phenyl esters have bends at the ends of the curves, pointing to a tendency for formation of a compound in the racemic form, there are no eutectic points and, hence, there is no formation of true *dl* compounds.

FIG. 3



The melting point composition diagrams of the rest of the compounds, *i.e.*, *o*- and *m*-chloro-(Fig. 1, curves 2 and 1), *o*- and *m*-bromo-(Fig. 2, curves 2 and 1) and *o*- and *p*-nitro-(Fig. 3, curves 1 and 3) phenyl esters consist each of three curves, DE_1, E_1RE_2 and E_2L, with a central maximum, R. This indicates that the racemic forms of the esters in question are *dl* compounds. The eutectic points are fairly well defined and sharp. The *dl*- and *d*- curves of *m*-bromo- and *o*- and *p*-nitro-phenyl esters are steep and cover large areas under them, whereas those of *o*- and *m*-chloro- and *o*- bromo-phenyl esters are not so steep and cover smaller areas under them, pointing to the fact that the racemates of the former group of esters are more stable than the racemates of the latter. The central portions of the curves, except in the case of *p*-nitrophenyl ester, are more or less

rounded, pointing to the dissociation of the *dl* compounds in the liquid state into optically active components.

The authors express their grateful thanks to Dr. Bawa Kartar Singh, Retired Honorary Research Professor and Head of the Organic Chemistry Research Section, for suggesting the problem and initiating them into this investigation and also to the Banaras Hindu University for the research facilities and the award of Research Assistantship to one of them (S.R.G. Sarma).

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BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES. PART VIII. PREPARATION OF SOME POLYNITROPHENYLHYDRAZINES, THEIR HYDRAZONES AND SOME 2-ARYLBENZOTRIAZOLES

By R. S. Kapil and S. S. Joshi

3-Chloro-4 :6-dinitro-, 2 :3-dichloro-4 :6-dinitro- and 2-chloro-3-bromo-4 :6 dinitro-phenylhydrazines have been obtained by replacing a halogen atom by a hydrazino group. Their hydrazones and several 2-arylbenzotriazoles have also been prepared.

The present investigation is an extension of the work published previously (Joshi and Deorha, this *Journal*, 1951, **28**, 34 ; 1952, **29**, 46 ; 1957, **34**, 14) and describes the preparation of some more polynitrophenylhydrazines. These have been obtained by the action of hydrazine hydrate on 1 :3-dichloro-4:6-dinitro- (Nietzki and Schedler, *Ber.*, 1897, **30**, 1666 ; Sane and Joshi, *J. Chem. Soc.*, 1924, **125**, 2481), 1 :2 :3-trichloro-4 :6-dinitro-(Joshi and Saxena, this *Journal*, 1953, **30**, 548) and 1:3-dibromo-2-chloro-4 :6-dinitro- (Joshi and Saxena, *loc.cit.*) benzenes in the cold.

The yields of the substituted polynitrophenylhydrazines are good. Their structure follows from the method of preparation. The hydrazones have been prepared by the usual methods.

The reaction between a reactive halogen compound and an arylphenylhydrazine furnishes 2-arylbenzotriazoles and their 1-oxides (Willgerodt and Ferko, *J. prakt. Chem.*, 1888, *ii*, **37**, 351 ; Joshi and Sane, this *Journal*, 1933, **10**, 459 ; Joshi and Gupta *ibid.*, 1958, **35**, 681). The formation of the product in this condensation, benzotriazole or its oxide, is considerably influenced by the reagents employed. Thus, phenylhydrazine and a reactive halogen compound in presence of alcohol or alcohol and sodium bicarbonate or sodium acetate afford a 2-aryl-1 :2 : 3-benzotriazole while in acetic acid solution, they form 2-aryl-1 : 2 : 3 benzotriazole-1-oxide.

Using this method, the condensation of 1 :3-dichloro-4 :6-dinitro-, 1 :2 :3-trichloro-4 :6-dinitro- and 1:3-dibromo-2-chloro-4 :6-dinitro-benzenes with phenyl- and *o*-tolylhydrazines has been studied and the corresponding 2-aryl-1 :2 :3-benzotriazoles and 1-oxides have been prepared.

Experimental*

3-Chloro-4 :6-dinitrophenylhydrazine was prepared according to Borsche (*J. prakt. Chem.*, 1925, *ii*, **16**, 138) in 80% yield, m.p. 198°. (Found : Cl, 14.41. Calc. for $C_6H_5O_4N_4Cl$: Cl, 15.27%).

* All melting points recorded are uncorrected.

TABLE I

S. No.	Carbonyl compound.	3-Chloro-4:6-DNP. M. P.	Colour.	% Chlorine. Found.	Calc.	2:3-Dichloro-4:6-DNP M. P.	Colour.	% Chlorine. Found	Calc.	2-Chloro-3-bromo-4:6-DNP. M. P.	Colour.	% Cl+Br. Found.	Calc.
1.	Benzaldehyde	243°	Orange-red	10.72	11.08	225°	Yellow	19.72	20 00	238°	Yellow	28.61	28.92
2.	Salicylaldehyde	**290°	Orange	9.97	10.55	203°	,,	18.86	19.14	300°(d)	Brown	27.49	27.81
3.	Anisaldehyde	**237°	Deep red	9.78	10.13	240°	,,	18.14	18.44	240°	Yellow	26.61	26.89
4.	Cinnamaldehyde	274°	Red	10.31	10.64	216°	Orange-red	18.94	19.30	208°	Orange-yellow	27 63	28.00
5.	*p*-Dimethylamino-benzaldehyde	265°	Brown	9.42	9.76	193°(d)	Dark red	17.62	17.84	211°	Dark red	25.84	26.10
6.	Acetophenone	**213°	Orange-yellow	10.22	10.61	150°	Yellow	18.73	19.24	187°	Light yellow	27.61	27.94
7.	*p*-Hydroxy-acetophenone	264°	Chocolate	9.56	10.13	208°	Brown	18.24	18.44	210°	Reddish brown	26.34	26.89
8.	3-Methyl-4-hydroxy-acetophenone	226°	Orange-yellow	9.31	9.73	175°	Dark brown	17.23	17.79	203°	Orange-yellow	25 76	26.04
9.	3-Chloro-2-hydroxy-5-methylacetophenone	238°	Red	17.45	17.79	228°	Red	24.16	24.57	231°	Red	31.22	31.59
10.	3-Bromo-2-hydroxy-5-methylacetophenone	245°	,,	(Cl+Br) 25.68	26.04	208°	,,	(Cl+Br) 31.28	31.59	215°	Deep red	37.03	37 41

DNP denotes dinitrophenylhydrazone.

** Roberts, *Rec. trav. chim.*, 1937, **56**, 413.

TABLE II

	Halo-4 :6-dinitrobenzene.	Phenylhydrazine used.	2-Aryl-1 :2 :3-benzotriazole formed.	M. P.	Colour.	Formula	% Chlorine. Found.	Calc.
1.	1 :3-Dichloro-	Phenylhydrazine	5-Chloro-6-nitro-	200°	Golden yellow	$C_{12}H_7O_2N_4Cl$	12.58	12.93
2.	Do	*o*-Tolylhydrazine	5-Chloro-6-nitro-	140°	Light yellow	$C_{13}H_9O_2N_4Cl$	12.06	12.30
3.	1 :2 :3-Trichloro-	Phenylhydrazine	4 :5-Dichloro-6-nitro-	197°	Buff needles	$C_{12}H_6O_2N_4Cl_2$	22.76	22.97
4.	Do	*o*-Tolylhydrazine	Do	159°	Colorless	$C_{13}H_8O_2N_4Cl_2$	21.64	21.99
5.	1 :3-Dibromo-2-chloro-	Phenylhydrazine	4-Chloro-5-bromo-6-nitro-	212°	Light buff needles	$C_{12}H_6O_2N_4ClBr$	% (Cl+Br).	
	Do	*o*-Tolylhydrazine					32.15	32.68
6.			Do	176°	Light brown needles	$C_{13}H_8O_2N_4ClBr$	31 24	31.43

TABLE III

S. No.	Halo-4 :6-dinitrobenzene used.	2-Phenyl-1 :2 :3-benzotriazole-1-oxide formed.	M.P.	Colour.	Formula.	% Chlorine. Found.	Calc.
1.	1 :3-Dichloro-	5-Chloro-6-nitro-	195°	Fawn leaflets	$C_{12}H_7O_3N_4Cl$	11.89	12.22
2.	1 :2 :3-Trichloro-	4 :5-Dichloro-6-nitro.	193°	Light buff needles	$C_{12}H_6O_3N_4Cl_2$	21.35	21.84
3.	1 :3-Dibromo-2-chloro-	4-Chloro-5-bromo-6-nitro-	181°	Light yellow	$C_{12}H_6O_3N_4ClBr$	% (Cl+Br). 30.85	31.26

2 : 3-*Dichloro*-4 : 6-*dinitrophenylhydrazine*.—1 : 2 : 3-Trichloro-4 : 6-dinitrobenzene, dissolved in excess of alcohol, was treated at room temperature with an equivalent quantity of hydrazine hydrate. On keeping for 24 hours at room temperature the phenylhydrazine derivative formed separated out ; it was purified from an excess of alcohol as greenish yellow needles (75%), m.p. 193°. (Found : Cl, 26.16. $C_6H_4O_4N_4Cl_2$ requires Cl, 26.59%).

2-*Chloro*-3-*bromo*-4 : 6-*dinitrophenylhydrazine* was prepared by the above procedure from 1 : 3-dibromo-2-chloro-4 : 6-dinitrobenzene and hydrazine hydrate as greenish yellow needles, (70%), m.p. 188°. (Found : Cl + Br, 36.61. $C_6H_4O_4N_4ClBr$ requires Cl + Br, 37.08%).

Phenylhydrazones were obtained in nearly quantitative yield by boiling for 4-5 minutes a mixture of the substituted phenylhydrazines (0.5 g.) in alcohol (10 c.c.) and the carbonyl compounds in equimolecular proportions in presence of H_2SO_4 (conc., 1 or 2 drops). These were recrystallised from ethyl acetate. Characteristics of hydrazones prepared are recorded in Table I.

2-*Aryl*-1 : 2 : 3-*benzotriazoles*.—Halogenodinitrobenzenes, dissolved in alcohol, and substituted phenylhydrazines (1 : 1.5) were heated on a water-bath. Soon after, shining crystals began to separate. After about half an hour the mass was cooled and filtered. The 2-aryl-1 : 2 : 3-benzotriazoles formed were recrystallised from alcohol (Table II).

2-*Phenyl*-1 : 2 : 3-*benzotriazole*-1-*oxides* were prepared by heating an acetic acid solution of the reactive halogen compounds and phenylhydrazine (1:1.5) on a water-bath for half an hour. The mass was cooled, filtered and recrystallised from toluene (Table III).

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ANTISPASMODIC COMPOUNDS. PART IV

By B. Sahoo, P. B. Tripathy and M. K. Rout

Several quinolylthiazoles, quinolylthionothiazolidines and quinolylthionoiminazolidines have been prepared for the study of their antispasmodic action and formulation, if possible, of any general relationship between antispasmodic action and nature of the heterocyclic nucleus present as well as that of substituents on it. The spasmolytic tests suggest the presence of musculotropic activity in most of the compounds

During recent years several synthetic drugs including some pyridylquinoline and thiazolylquinoline derivatives possessing pronounced antispasmodic activity have been discovered (Coates *et al.*, *J. Chem. Soc.*, 1943, 401, 419 ; Heilbron *et al.*, *ibid.*, 1949, 419).

In view of the observed spasmolytic action of the quinoline system, it was considered of interest to link the quinoline nucleus to some chemotherapeutically active heterocyclic nucleus like thiazoles, thionothiazolidine and thionoiminazolidine (the latter two were derived from rhodanine and thiohydantoin respectively). Thiazoles, rhodanines and thiohydantoins were taken up for investigation on account of their ability to promote antispasmodic activity (Chance *et al.*, *Brit. J. Pharmacol.*, 1946, **1**, 153 ; Blicke and Taso, *J. Amer. Chem. Soc.*, 1944, **66**, 1645 ; Anderson and Green, *Nature*, 1950, **165**, 122).

In the present investigation, the preparation of several quinolylthiazoles, quinolylthiazolidines and quinolyliminazolidines was therefore undertaken with the object of studying the antispasmodic activity with variation in the nature of the heterocyclic nucleus. It was also desired to examine the effect of changing substitution on the heterocyclic nucleus.

In our investigation, quinolylthiazolidines have been prepared by two different methods (vide Experimental). The quinolyliminazoles were also synthesised by the above two methods, by replacing rhodanines by 3-aryl-2-thiohydantoin in the above reactions. The quinolylthiazoles were prepared as described by Rout *et al.* (this *Journal*, 1958, **35**, 407).

The preliminary screening made on isolated strips of rabbit small intestine, by measuring the decrease of normal rhythmic contraction of the intestine, revealed that most of the drugs possessed to some extent musculotropic activity. The detailed results will be published elsewhere.

Experimental

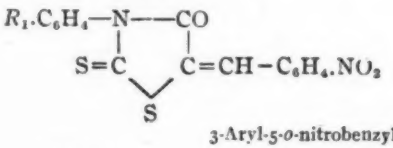
N-Arylrhodanines were prepared by the reaction of sodium monochloroacetate with the respective ammonium aryldithiocarbamates. The properties and analytical data of these are recorded in Table I.

o-Nitrobenzylidene-rhodanines (II) : *3-Phenyl-5-o-nitrobenzylidene-rhodanines.*—To a solution of *o*-nitrobenzaldehyde (0.6 g.) and *N*-phenylrhodanine (1 g.) in hot glacial

acetic acid (20-30 c.c.) fused sodium acetate was added and the mixture was refluxed for nearly 2½ hours on an asbestos-centered wire-gauze with occasional shaking. On cooling, the reaction mixture was poured to a large volume of water, when a yellow precipitate was obtained. It was kept overnight, filtered and washed with water. Finally it was crystallised from alcohol, m.p. 238-40°, yield 80%. (Found: N, 8.03; S, 18.7. $C_{16}H_{10}O_3N_2S_2$ requires N, 8.19; S, 18.89%).

The properties and analytical data of other compounds of this series are described in Table I.

TABLE I



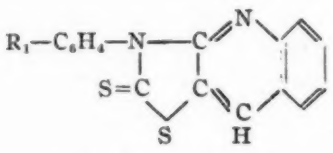
3-Aryl-rhodanines. 3-Aryl-5-*o*-nitrobenzylidene-rhodanine.

			% Sulphur.				% Sulphur.	
R_1.	Yield.	M. P.	Found.	Calc.	Yield.	M.P.	Found.	Calc.
p-Me	63%	158-59°	28.25	28.70	70.0%	180°	18.06	17.98
m-Me	65	149°	28.47	28.70	82.0	175-76°	17.86	17.98
o-Me	60	105°	28.35	28.70	85.5	168-70°	17.89	17.98
p-Cl	62	155-56°	26.01	26.28	85.0	198-99°	16.85	17.00
m-Cl	54	165°	25.97	26.28	73.0	180-81°	17.06	17.00

2-*Thiono*-3-*phenyl*-4 : 5-(2′ : 3′)-*quinolylthiazolidine* (III).—A solution of 3-phenyl-5-*o*-nitrobenzylidene-rhodanine (3 g.) in 20 c.c. of glacial acetic acid was heated under reflux with zinc dust until it became nearly colorless. (A slight yellow tinge remained in some cases even after heating for 19 hours). The mixture was filtered and the filtrate was diluted with a large excess of water, when a white precipitate gradually settled down; this was separated by filtration, and was washed with HCl (dil.) followed by water. The precipitate was extracted with hot alcohol and finally recrystallised from alcohol, m.p. 108-10°, yield 40%. (Found: N, 9.65; S, 21.59. $C_{16}H_{10}N_2S_2$ requires N, 9.52; S, 21.77%).

The properties and analytical data of other compounds of this series are recorded in Table II.

TABLE II

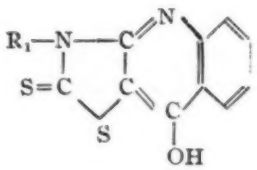


			% Sulphur.	
Nature of R_1.	Yield.	M.P.	Found.	Calc.
p-$CH_3.C_6H_4$	35%	120-22°	19.86	20.15
m-$CH_3.C_6H_4$	32	255 (d)	19.75	20.15
o-$CH_3.C_6H_4$	30	138-40°	20.05	20.15
p-$Cl.C_6H_4$	33	245° (d)	18.6	18.58
m-$Cl.C_6H_4$	32	108-10°	18.43	18.58

2-Thiono-3-phenyl-4 : 5-(2′ : 3′)-4-hydroxyquinolylthiazolidine (IV).—A mixture of 3-phenylrhodanine (2.1 g.) and anthranilic acid (1.37 g.) was fused at 150° and finely powdered sodium acetate (anhydrous, 1.20 g.) was slowly added, such that the addition was completed in 1 hour. The mass was heated for a further period of 5 hours at 130-40°. On cooling, it was treated with aqueous sodium bicarbonate solution, in which the unchanged anthranilic acid dissolved. It was next filtered and the filtrate was treated with cold dilute alkali. A small portion which remained undissolved was separated by filtration. The alkaline filtrate on acidification with HCl (dil.) yielded a yellow precipitate. It was filtered and crystallised from alcohol, m.p. 280°, yield 56%. (Found : N, 9.09 ; S, 20.53. $C_{16}H_{10}ON_2S_2$ requires N, 9.03 ; S, 20.65%).

The properties and analytical data of other compounds of this series are recorded in Table III.

TABLE III



Nature of R_1.	Yield.	M.P.	% Sulphur. Found.	Calc.
p-$CH_3.C_6H_4$	54.0%	280°	19.71	19.75
m-$CH_3.C_6H_4$	56.0	300°	19.45	19.75
o-$CH_3.C_6H_4$	57.5	250°	19.81	19.75
p-Cl.C_6H_4	53.0	250°	18.47	18.58
m-Cl C_6H_4	56.0	293°	18.62	18.58

3-p-Tolyl-5-o-nitrobenzylidene-2-thiohydantoin.—*o*-Nitrobenzaldehyde (11.51 g.) and *p*-tolylthiohydantoin (1.93 g.) were refluxed in glacial acetic acid in presence of fused sodium acetate (2 g.) on an asbestos-centred wire-gauze. The compound was isolated in the same manner as compound (II), m.p. 195°, yield 50%. (Found : S, 9.22. $C_{17}H_{13}O_3N_3S$ requires S, 9.44%).

2-Thiono-3-p-tolyl-4 : 5 (2′ : 3′)-quinolyliminazolidines (VI).—A solution of 3-*p* tolyl-5-*o*-nitrobenzylidene-2-thiohydantoin (3 g.) in 20 c.c. of glacial acetic acid was refluxed in presence of zinc dust. After refluxing for 10 hours, the solution became nearly colorless. The desired compound was isolated as described in the case of compound (III), m.p. 223°, yield 42%. (Found : S, 10.82. $C_{17}H_{13}N_3S$ requires S, 11.00%).

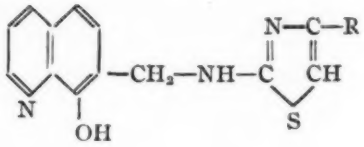
2-Thiono-3-p-tolyl-4 : 5-(2′ : 3′)-4′-hydroxyquinolyliminazolidine (VII) was prepared in the same way as compound (IV) from 3-*p*-tolyl-2-thiohydantoin (1.93 g.) and anthranilic acid (1.3 g.), m.p. 232° (decomp.), yield 55%. (Found : S, 10.31. $C_{17}H_{13}ON_3S$ requires S, 10.42%).

4-p-Hydroxyphenyl-2-(8′-hydroxy-7′-quinolinyl)-methylaminothiazoles (VIII).—A mixture of 8-hydroxyquinoline (1.46 g.), paraformaldehyde (1.2 g.) and 4-*p*-hydroxyphenyl-2-aminothiazole (2.08 g.) with alcohol (20 c.c.) and HCl (conc., 2 c.c.) was

refluxed for 8 hours. Excess of alcohol was removed and the syrupy mass on treatment with a large volume of water furnished a pasty mass, which solidified on keeping in contact with ammonia. It was crystallised from alcohol, m.p. 152° (decomp.), yield 65%. (Found : S, 8.74. $C_{19}H_{15}O_2N_3S$ requires S, 9.1%).

The properties and analytical data of other compounds of this series are shown in Table IV.

TABLE IV



Nature of R.	Yield.	M.P.	% Sulphur. Found.	Calc.
p-OH, *m*-OMe C_6H_3	68%	135°	8.04	8.42
p-$C_{10}H_7$	70	128°	8.46	8.80

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*iso*QUINOLINE DERIVATIVES. PART V

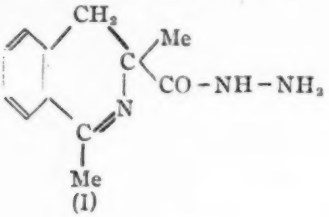
By T. N. Ghosh and Bhabatosh Bhattacharya

Ethyl α-methyl-α-acylamido-β-phenylpropionate (III), when subjected to the Bischler-Napieralski cyclisation in an inert solvent with phosphorus pentoxide, one of the standard agents, yields the corresponding 1-aryl-3-methyl*iso*quinoline, the process apparently involving cyclodehydration, hydrolysis of the carbethoxy group, decarboxylation and dehydrogenation

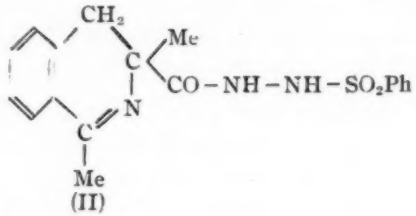
Attempts were previously made from this laboratory to introduce aliphatic amine chain into the 3-position of 3-methyl-3 : 4-dihydro*iso*quinoline derivatives, so that the resulting compounds could be tested for any spasmolytic activity. A new approach in this direction envisages preparation of 3-methyl-3 : 4-dihydro*iso*quinoline-3-aldehyde, which might constitute a suitable starting material for the above purpose. 1 : 3-Dimethyl-3-carbethoxy-3 : 4-dihydro*iso*quinoline (Ghosh *et al.*, this *Journal*, 1958, **35**, 758) has been converted into the corresponding hydrazide (I), which, on treatment with benzenesulphonyl chloride in pyridine, has furnished the sulphonyl derivative (II). Attempts to convert (II) into the corresponding 3-aldehyde by treatment with sodium carbonate in ethyleneglycol or glycerine (cf. McFadyen and Stevens, *J. Chem. Soc.*, 1936, 584 ; Buchman and Richardson, *J. Amer. Chem. Soc.*, 1939, **61**, 892) have failed. A liquid of indefinite boiling point (90-150°/5 mm) has been obtained, which does not show the characteristic property of an aldehyde.

In order to prepare 1-phenyl-3-methyl-3-carbethoxy-3 : 4-dihydro*iso*quinoline and subject the same to the reactions as outlined above, α-methyl-α-benzamido-β-phenylpropionic acid (Ghosh *et al.*, this *Journal*, 1957, **34**, 417) has been esterified and the ethyl ester (III, R = Ph) treated with phosphorus oxychloride in an inert solvent, when, to the exclusion of any basic compound, the azlactone (IV : R = Ph) has been obtained. By employing, however, phosphorus pentoxide in presence of an inert solvent, (III : R = Ph) has furnished a base found to be 1-phenyl-3-methyl*iso*quinoline (V : R = Ph). Snyder and Werber (*J. Amer. Chem. Soc.*, 1950, **72**, 2962) have observed that when *N*-acetylphenylalanine is subjected to the Bischler-Napieralski reaction with a mixture of polyphosphoric acid and phosphorus oxychloride, 1-methyl*iso*quinoline is formed, the process involving cyclodehydration, decarboxylation and dehydrogenation. Neither polyphosphoric acid nor phosphorus oxychloride alone can bring about this reaction, but rather drastic condition, involving the use of a mixture of these two agents, is needed. It is therefore significant to note the facile way in which the conversion of (III : R = Ph) to (V : R = Ph) is taking place under the influence of phosphorus pentoxide, the process apparently involving cyclodehydration, hydrolysis of the carbethoxy group, decarboxylation and dehydrogenation. That this reaction with such structure as (III : R = Ph) appears to be a general one is exemplified by the observation now made that, when ethyl α-methyl-α-acetamido-β-phenylpropionate (III : R = Me) and ethyl α-methyl-α-phenylacetamido-β-phenylpropionate (III : R = CH_2Ph)

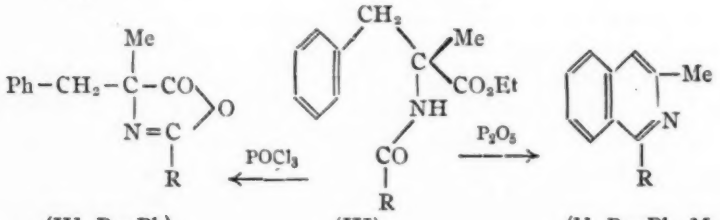
are similarly treated with phosphorus pentoxide, 1 : 3-dimethyl*iso*quinoline (V R=Me) and 1-benzyl-3-methyl*iso*quinoline (V : R=CH_2Ph) respectively are obtained. The obvious difference in structure of the compound employed by Snyder and Werber (*loc. cit.*) and of the ones in the present case lies in the presence of a quaternary carbon atom in the latter. This raises the issue whether the presence of a quaternary carbon atom in such a position in these compounds promotes this facile reaction, and in order to establish this point more data are needed.



(I)



(II)



(IV : R=Ph) (III) (V : R=Ph, Me, CH_2Ph)

In connection with the above *iso*quinoline derivatives, it is to be noted that there is some discrepancy in the literature about the melting points of the base (V : R=Ph) and of its derivatives. This base, however, has been obtained by other workers through different routes. While our findings are in close agreement with those of Dobrowsky (*Monatsh.*, 1951, **82**, 122), these are in some cases at variance with those of Whaley and Hartung (*J. Org. Chem.*, 1949, **14**, 650).

EXPERIMENTAL

1 : 3-*Dimethyl*-3 : 4-*dihydro*isoquinoline-3-*carboxylic Acid Hydrazide* (I).—A mixture of 1 : 3-dimethyl-3-carbethoxy-3 : 4-dihydro*iso*quinoline (4.62 g.) and hydrazine hydrate (2 g., 60%) in ethanol (25 c.c., 95%) was refluxed for 3 hours. On cooling, the clear solution furnished a solid which was recrystallised from ethanol in colorless rhombic crystals, m.p. 164-65°. (Found : N, 18.98. $C_{12}H_{15}ON_3$ requires N, 19.35%).

1 : 3-*Dimethyl*-3 : 4-*dihydro*isoquinoline-3-*benzenesulphon-carboxylic Acid Hydrazide* (II).—To a suspension of (I, 8.71 g.) in pyridine (115 c.c.) was added under stirring benzenesulphonyl chloride (10 g.) over a period of 1 hour, the temperature being maintained at about 20°. The resulting violet solution was stirred for about 3 hours and the pyridine distilled off from a steam-bath under reduced pressure. The residual mass was poured into water when a pinkish solid (13 g.) separated. It was crystallised from methanol in colorless microcrystalline powder, m.p. 202-203°. Found : N, 11.52. $C_{18}H_{19}O_3N_3S$ requires N, 11.76%).

Azlactone (IV : R = Ph) *of α Methyl-α-benzamido-β-phenylpropionic Acid.*—A mixture of α-methyl-α-benzamido-β-phenylpropionic acid (23.5 g.), H_2SO_4 (conc., 1.13 c.c.) and anhydrous ethanol (110.2 c.c.) was heated under reflux for 8 hours. After removal of ethanol, the residue was poured into water when the ester separated as an oil, which gradually solidified and was crystallised from ethanol in colorless needles, m.p. 118-19°. (Found : N, 4.52. $C_{19}H_{21}O_3N$ requires N, 4.50%).

A mixture of the above ester (III : R = Ph ; 7 g.), benzene (70 c.c.) and $POCl_3$ (7 c.c.) was heated under reflux on the steam-bath for 4 hours. Benzene was removed by distillation under reduced pressure and the residue, on basification with cold dilute alkali solution, yielded a semisolid mass, which was purified by trituration with ether and crystallised from ethanol in colorless needles, m.p. 200-201°. (Found : N, 5.08. $C_{17}H_{15}O_2N$ requires N, 5.28%).

It is insoluble in HCl (dil.) and in cold dilute alkali. It was hydrolysed by keeping at room temperature for 5 to 6 hours with aqueous NaOH solution (10%) to afford, on acidification of the clear solution, α-methyl-α-benzamido-β-phenylpropionic acid.

Treatment of Ethyl α-Methyl-α-benzamido-β-phenylpropionate (III : R = Ph) *with* P_2O_5 : *Formation of 1-Phenyl-3-methylisoquinoline* (V : R = Ph).—A mixture of (III : R = Ph ; 8 g.), P_2O_5 (32 g.) and xylene (160 c.c.) was heated under reflux in an oil-bath for 5 to 6 hours. After removal of xylene under reduced pressure, the residue was treated with ice-water, and basified with alkali, when the base was obtained as a semisolid mass, which soon solidified. It was purified by acid-alkali treatment and crystallised from aqueous ethanol in colorless plates, m.p. 90-91°. Dobrowsky (*loc. cit.*) records m.p. 90°, while Whaley and Hartung (*loc. cit.*) record m.p. 123-25°. The compound was unaffected, when heated over palladium-charcoal in tetralin at 250° in CO_2 atmosphere or when heated with sulphur in tertalin at 200-205°. (Found : N, 6.12. $C_{16}H_{13}N$ requires N, 6.39%). The *hydrochloride* was obtained in colorless plates, m.p. 229°. (Found : N, 5.63. $C_{16}H_{13}N.HCl$ requires N, 5.48%). Whaley and Hartung (*loc. cit.*) record 229° as the m.p. of the hydrochloride and Dobrowsky (*loc. cit.*) records m.p. 228°. The *picrate* was crystallised from ethanol in yellow needles, m.p. 200-201°. (Found : C, 58.62 ; H, 3.48 ; N, 12.71. $C_{16}H_{13}N.C_6H_3O_7N_3$ requires C, 58.93 ; H, 3.57 ; N, 12.50%). Whaley and Hartung (*loc. cit.*) record 188° as the m.p. of the picrate.

Treatment of Ethyl α-Methyl-α-acetamido-β-phenylpropionate (III : R = Me) *with* P_2O_5 : *Formation of 1 : 3-Dimethylisoquinoline* (V : R = Me).—The procedure was the same as described above. The base was obtained as an oil and was characterised as picrate, crystallising from ethanol in yellow needles, m.p. 181-82°, undepressed on admixture with an authentic sample (Witkop, *J. Amer. Chem. Soc.*, 1948, **70**, 1424). (Found : N, 14.52. Calc. for $C_{11}H_{11}N.C_6H_3O_7N_3$: N, 14.51%).

Ethyl α-Methyl-α-phenylacetamido-β-phenylpropionate (III : R = CH_2Ph).—α-Methyl-α-amino-β-phenylpropionic acid (35.8 g) was heated on the steam-bath for about 5 hours with phenylacetic anhydride (48 g.) and dry pyridine (60 g.). Pyridine was removed by steam distillation. The lower oily layer was separated and boiled with a large volume

of water when a colorless solid (15 g.) precipitated on cooling. The acid was crystallised from aqueous ethanol in colorless needles, m.p. 167-68°. (Found : N, 4.84. $C_{18}H_{19}O_3N$ requires N, 4.71%).

The *ethyl ester* was prepared in the usual way with EtOH-H_2SO_4 and was crystallised from aqueous ethanol in colorless needles, m.p. 96-97°. (Found : N, 4.48. $C_{20}H_{23}O_3N$ requires N, 4.31%).

Treatment of (III : R=CH_2Ph) *with* P_2O_5 : *Formation of* 1-*Benzyl*-3-*methyl*iso*quinoline* (V : R=CH_2Ph). – The procedure was the same as described above. After removal of xylene under reduced pressure, the reaction mass was treated with ice-water when a pasty mass* separated. The aqueous solution, on basification with alkali, liberated the base as an oil. The *hydrochloride* was crystallised from water in colorless needles, m.p. 228°. (Found : N, 5.18. $C_{17}H_{15}N.HCl$ requires N, 5.19%). Dobrowsky (*loc. cit.*) records m.p. 222°. Whaley and Hartung (*loc. cit.*) record m.p. 207° (decomp.).

The *hydrobromide* was crystallised from water in colorless needles, m.p. 250-51°. (Found : N, 4.47. $C_{17}H_{15}N.HBr$ requires N, 4.46%).

The *picrate* was crystallised from ethanol in yellow needles, m.p. 197-98°. (Found : C, 59.26 ; H, 3.91 ; N, 12.31. $C_{17}H_{15}N.C_6H_3O_7N_3$ requires C, 59.74 ; H, 3.89 ; N, 12.12%).

The pasty mass, mentioned above (marked with an asterisk), solidified on standing and it was crystallised from aqueous ethanol as a colorless microcrystalline powder, m.p. 224-25°. It is sparingly soluble in water and has been characterised as the *diphosphate* of the base (V : R=CH_2Ph). (Found : N, 3.52 ; P, 15.5. $C_{17}H_{15}N.2H_3PO_4$ requires N, 3.26 ; P, 14.45%).

The authors are grateful to Dr. U. P. Basu, Director of the Institute, for his continued interest.

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ORGANIC REACTIONS WITH POLYPHOSPHORIC ACID. PART VI.* INTRAMOLECULAR ACYLATION WITH LACTONES: *cyclo*PENTENONES FROM δ-LACTONES

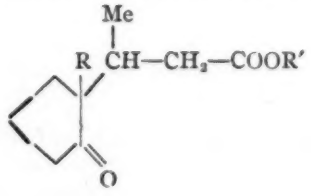
By T. M. Jacob and Sukh Dev

The scope of the previously described method for the synthesis of bi*cyclo*-[0 : 3 : 3]-octane and bi*cyclo*-[0 : 3 : 4]-nonane systems has been further extended to compounds substituted in the newly formed 5-membered ring.

It has been shown previously (Rai and Sukh Dev, this *Journal*, 1957, **34**, 178 ; Sukh Dev and Rai, *ibid.*, 1957, **34**, 266) that the intramolecular acylation of properly constituted γ-lactones and δ-lactones in the presence of polyphosphoric acid (PPA) can be used as a convenient method for the synthesis of *cyclo*pentenones. The method has now been extended to the preparation of 4-methyl-bi*cyclo*-[0 : 3 : 3]-$\Delta^{1:5}$-octen-2-one (I) and 4-methyl-bi*cyclo*-[0 : 3 : 4]-$\Delta^{1:5}$-nonen-2-one (IV).

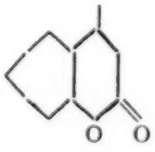
*cyclo*Pentene and crotonic acid react in the presence of PPA to yield a bicyclic ketone which has been characterised (Sukh Dev, this *Journal*, 1957, **34**, 169) as 4-methyl-bi*cyclo*-[0 : 3 : 3]-$\Delta^{1,5}$-octen-2-one (I). Since the properties of this ketone as well as those of its dihydro derivative differ somewhat from those of a preparation by Nazarov and Burmistrova (*Bull. Acad. Sci., U. S. S. R., Cl. Sci. Chim.*, 1947, 51), a straightforward synthesis of (I), using the previously developed PPA-induced intramolecular acylation of δ-lactones, has been carried out.

The Michael addition of ethyl crotonate to ethyl *cyclo*pentanone-2-carboxylate was best carried out in the presence of potassium butoxide, without any danger of the scission of the *cyclo*pentanone ring (Sukh Dev, *Science & Culture*, 1950, **16**, 31 ; cf. Bhattacharya, this *Journal*, 1945, **22**, 215), to yield (IIa). On hydrolysis it smoothly furnished the required δ-keto-acid (IIb) ; this was reduced either by the sodium borohydride method (Chaikin and Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 122) or by the the Raney nickel alloy-alkali method (Schwenk *et al.*, *J. Org. Chem.*, 1944, **9**, 175) to afford the hydroxy-acid, which in the presence of acid lactonised to yield the δ-lactone (III). The lactone (III) on treatment with PPA afforded 94-96% yield of the required ketone (I), which was found to be completely identical with the material prepared earlier by the reaction of *cyclo*pentene and crotonic acid in the presence of PPA (*loc. cit.*). The overall yield of (I) by this method was about 66%.

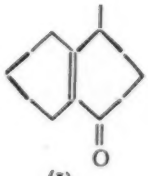


(II)

[a : R = COOEt ; R' = Et.
b : R = R' = H.]



(III)

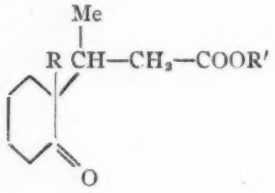


(I)

*Part V, this journal, 1957, **34**, 266.

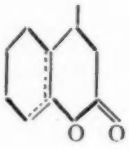
By using ethyl *cyclo*hexanone-2-carboxylate, instead of the *cyclo*pentanone carboxylate, 3-methyl-4:5:6:7-tetrahydroindan-1-one (IV) (cf. Nazarov and Pinkina, *Bull. Acad. Sci., U.S.S.R., Cl. Sci. Chim.*, 1946, 633; Hamlet *et al.*, *J. Chem. Soc.*, 1951, 2652; Braude and Coles, *ibid.*, 1952, 1430; Sukh Dev, *loc. cit.*) was next, likewise, synthesised in an overall yield of about 30%. During this synthesis, a few peculiarities have been observed, which deserve mention.

Under the Michael addition conditions, which furnished (IIa) in 73% yield, the *cyclo*hexanone analogue (Va) could only be obtained in 50% yield. An improvement in the yield was noticed by increasing the base concentration, but the effect was small. During the distillation of the keto-acid (Vb), a lower-boiling fraction was always obtained; this decolorised bromine in carbon tetrachloride and could be converted into the keto-acid (Vb) on base treatment, and on the basis of these it has been formulated as the enol-lactone (VI).

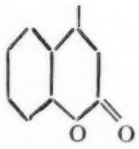


(V)

[a: R = COOEt; R' = Et.
b: R = R' = H.]



(VI)



(VII)

(IV)

Unlike the *cyclo*pentanone analogue, the PPA-induced acylation of the lactone (VII) to the tetrahydroindanone was found to be incomplete under a variety of conditions (Table I) similar to that observed previously (Sukh Dev and Rai, *loc. cit.*) with the non-methylated systems.

TABLE I

Intramolecular acylation of (VII).

No.	Temp.	Time.	Yield*.	% Ketone content.	Absolute yield of the ketone based on the lactone.
1	60° ± 2°	3 hrs.	0.68 g.	57.25	51.9%
2	,,	6	0.66	64.30	56.6
3	,,	9	0.70	66.70	62.3
4	80° ± 2°	3	0.70	78.00	72.8
5	,,	6	0.60	78.50	62.8

* Yield of the distillable material (b.p. 130-160°/15 mm) from a PPA reaction using 0.84 g. (0.0:5 *M*) of the lactone.

EXPERIMENTAL**

Ethyl β-(2-Carbethoxycyclopentanone)-butyrate (IIa).—A mixture of ethyl *cyclo*pentanone carboxylate (15.6 g., 0.1 *M*) and ethyl crotonate (11.4 g., 0.1 *M*) was added in

**Melting and boiling points are uncorrected. The spectra were measured in 95% ethanolic solution on a Beckman DU spectrophotometer.

one lot to an ice-cooled solution of potassium (0.78 g., 0.02 g. atom) in butanol^t (30 c.c.); butanol^t (25 c.c.) was used for washing in the last traces of the reactants. This was allowed to stand at room temperature (23°) for 16 hours and then gently refluxed for 12 hours. On cooling down, acetic acid (4 c.c.) and water (10 c.c.) were added and the product was taken up in ether (40 c.c. × 2). The extract was washed with brine (40 c.c. × 2) and dried. After removal of the solvent the residue was fractionated to furnish the required product as a colorless liquid, b.p. 145-47°/1.5 mm, n_D^{27} 1.4560, yield 19.85 g. (73.5%) (Bhattacharyya, *loc. cit.*, reports b.p. 158-60°/5 mm).

β-(2-Oxocyclopentyl)-butyric Acid (IIb).—The above ester (18 g.), HCl (C.P., 36 c.c.) and water (18 c.c.) were mixed and refluxed in a metal bath at 150-60° for 16 hrs. The excess of aqueous acid was removed from a steam-bath under suction and the residue directly distilled off to afford a colorless viscous liquid, b.p. 154-55°/1.9 mm, $n_D^{25\cdot5}$ 1.4790, yield 10.8 g. (95.5%) (Bhattacharyya, *loc. cit.*, reports b.p. 154°/4 mm).

The *ethyl ester* was prepared by the H_2SO_4-EtOH method; b.p. 124°/2.5 mm, n_D^{25} 1.4560, yield 90% (Bhattacharpya, *loc. cit.*, reports b.p. 117°/4 mm).

β-Methyl-γδ-cyclopent no-δ-valerolactone (III): (*i*). *Sodium Borohydride Method.*—The keto-acid (IIb) (1.3 g., 0.0076 *M*) was dissolved in a solution of sodium bicarbonate (0.75 g., 0.0089 *M*) in water (6 c.c.). This was cooled in ice-water and sodium borohydride (0.12 g., 0.003 *M*) was added. The reaction mixture was kept at the ice-bath temperature for 2 hours and then at room temperature for another 16 hours. This was acidified with HCl (conc.) to *p*H 2 and warmed on the steam-bath for 30 minutes. It was then cooled, the product taken up in ether (10 c.c. × 6) after saturating with sodium chloride, washed with brine containing sodium bicarbonate (15 c.c. × 2) and dried. The solvent was distilled off (column) and the residue fractionated to furnish a colorless liquid, b.p. 120-25°/2.5 mm, $n_D^{25\cdot5}$ 1.4775, yield 0.73 g. (62%). An analytical sample had $n_D^{29\cdot5}$ 1.4785, $d_4^{29\cdot5}$ 1.0470, M_D 41.69 (calc. 41.02). (Found: C, 70.21; H, 9.33. $C_9H_{14}O_2$ requires C, 70.13; H, 9.09%).

The reduction of the *keto-ester* (4 g, 0.02 *M* in 15 c.c. of ethanol) was carried out with sodium borohydride (0.38 g., 0.01 *M* in 10 c.c. of ethanol) at room temperature for 20 hrs. The crude hydroxy-ester was hydrolysed with ethanolic KOH (50 c.c., 5%) for 4½ hours and worked up as above to yield 2.3 g. (74%) of the desired lactone; n_D^{27} 1.4770.

(*ii*). *Raney Nickel Alloy-alkali Method.*—To a well-stirred solution of the keto-acid (1.34 g., 0.0079*M*) in aq. NaOH (40 c.c., 10%) Raney nickel alloy (-40 mesh; 2 g.) was added in small lots during 1½ hrs. After stirring for another 7 hours at room temperature, it was filtered and the filtrate acidified with warm H_2SO_4 (10 c.c. in 25 c.c. water). This was left overnight and the product taken up in ether (15 c.c. × 4) and worked up as above, b.p. 124-25°/2.5 mm, $n_D^{29\cdot5}$ 1.4775, yield 1.2 g. (98.9%).

4-Methyl-bicyclo-[0:3:3]-$\Delta^{1:5}$-*octen-2-one* (I).—To PPA (from P_2O_5 21 g. and 85% syrupy phosphoric acid, 9 c.c. Sukh Dev, this *Journal*, 1955, **32**, 262) at 60° ± 2°, the above lactone (2.31 g., 0.015 *M*) was added in one lot, mixed thoroughly with a glass

rod and the resulting yellow reaction mixture heated at the above temperature for 5½ hours with occasional swirling under anhydrous conditions. The resulting dark greenish red product was treated with crushed ice and diluted further with ice-water to 120 c.c. (*ca.*), supersaturated with ammonium sulphate (60 g.) and continuously extracted with petroleum ether for 48 hrs. The extract was freed of the solvent and the residue distilled to furnish the ketone as a colorless liquid, b.p. 117°/18 mm, n_D^{24} 1.5060, yield 1.95 g. (95.5%) ; $\lambda_{max}^{alc.}$ 240 mμ (ε 12, 600). (Sukh Dev, *loc. cit.*, records b.p. 91-92°/4 mm, n_D^{24} 1.5045, $\lambda_{max}^{alc.}$ 241 mμ, ε 12,100). (Found : C 79.91 ; H, 8.92. $C_9H_{12}O$ requires C, 79.41 ; H, 8.9%).

The 2 : 4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method (crude ; m.p. 192-94°) and on two recrystallisations from glacial acetic acid-ethanol afforded fine dark red needles, m.p. 214-15°, mixed m.p. with the previous sample (Sukh Dev, *loc. cit.*, reports m.p. 214-15°) remained undepressed.

Ethyl β-(2-Carbethxoycyclohexanone)-butyrate (Va)—A mixture of ethyl *cyclo*-hexanone carboxylate (8.5 g., 0.05 *M*) and ethyl crotonate (5.7 g., 0.05 *M*) were added in one lot to an ice-cooled solution of potassium butoxide[f] (from 0.63 g., 0.016 g. atom of potassium) in butanol[f] (25 c.c.) ; the butanol[f] (15 c.c.) was used for washing in the last traces of the reactants. After being left overnight (16 hrs.) at room temperature (25°), the reaction mixture was refluxed for 8 hours and then worked up as described for (IIa) to afford the required product as a colorless liquid, b.p. 158-59°/2 mm, n_D^{28} 1.4625, yield 58%. An analytical sample had b.p. 158-59°/2 mm, $n_D^{29.5}$ 1.4630, $d_4^{29.5}$ 1.080, M_D 72.43 (calc. 72.58). (Found : C, 63.30 ; H, 8.48. $C_{15}H_{24}O_5$ requires C, 63.39 ; H, 8.45%).

β-(2-Oxocyclohexyl)-butyric Acid (Vb).—The above ester (Va, 18.25 g.) was mixed with HCl (C.P., 90 c.c.) and glacial acetic acid (36 c.c.) and the whole refluxed in an oil-bath at 145-60° for 48 hours (hood). The excess of HCl-AcOH was removed from the water-bath under suction. The cooled residue was taken up in aq. NaOH (ice-cold, 10%) and washed with ether. The alkaline solution was acidified with phosphoric acid and extracted with ether (50 c.c. × 4) ; the extract was washed with brine and dried. After removal of the solvent the residue was efficiently fractionated and the required product was collected as a viscous liquid, b.p. 156-57°/1.5 mm, n_D^{24} 1.4818, yield 9.3 g. (78%). (Found : C, 64.92 ; H, 9.26 ; neut. equiv., 181.3. $C_{10}H_{16}O_3$ requires C, 65.22 ; H, 8.69% ; neut. equiv., 184).

The 2 : 4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and after several days the precipitated derivative was collected from the reaction mixture and recrystallised from dilute alcohol to provide yellow leaflets, m.p. 98-100°. The analysis revealed the esterification of the carboxyl group. (Found : N, 14.58. $C_{18}H_{24}O_6N_4$ requires N, 14.28%).

During distillation of the keto-acid, invariably, a forerun (b.p. 100-103°/1.5 mm) was obtained in different amounts in different experiments. The product dissolved in sodium hydroxide solution and on acidification yielded (Vb). An analytical sample had b.p. 123°/3 mm, $n_D^{20.5}$ 1.4930. (Found : C, 71.72 ; H, 8.64. $C_{10}H_{14}O_3$ requires C, 72.3 ; H, 8.43%).

When the hydrolysis procedure detailed for (IIa) was applied to (Va), the main product (b.p. 185-200°/0.05 mm) gave a neutral equivalent of 246, indicating that the tertiary carbethoxy group remained mostly unsaponified.

β-Methyl-γδ-cyclohexano-δ-valerolactone (VII): (*i*) *Sodium Borohydride Reduction.*—The above keto-acid (Va) (1.15 g., 0.006*M*) was reduced with sodium borohydride (0.1181 g, 0.003 *M*) in aqueous sodium bicarbonate (0.525 g., 0.006 *M* in 6 c.c. water) by following the procedure recorded for the *cyclo*pentane analogue (II b). The lactone was collected as a colorless liquid, b.p. 135°/2.5 mm, $n_D^{25.5}$ 1 4870, yield 0.85 g. (90.5%). An analytical sample had n_D^{31} 1.4870, d_4^{31} 1.0710, M_D 45.13 (calc. 45.63). (Found : C, 71.52 ; H, 9.52. $C_{10}H_{16}O_2$ requires C, 71.44 ; H, 9.52%).

(*ii*) *Reduction with Raney Nickel Alloy and Alkali.*—The keto-acid (1.87 g., 0.0102 *M*) was reduced by the method used for (IIb), using NaOH (6 g. in 60 c.c. water) and Ni-Al alloy (3 g.). The yield of the product (b.p. 120°/1 mm, n_D^{26} 1.4855) was 1.55 g. (91%).

4-*Methyl* - *bicyclo* - [0 : 3 : 4]-$\triangle^{1:5}$-*nonen*-2 - *one* (IV).—The above lactone (VII) (0.84 g , 0.005 *M*) was treated with polyphosphoric acid (syrupy phosphoric acid 3 c.c. + 7 g. P_2O_5) at 60 or 80° for different periods of time and worked up as described for (I) except that the extraction was not carried out continuously. The ketone content of the distillate was determined as described elsewhere (Sukh Dev and Rai, *loc. cit.*). A check with a pure specimen of (IV) provided a ketone content of 99.5%.

It was not possible to separate the ketone (IV) from the lactone (VII) completely by fractionation. The following method was adopted to effect the separation. The crude ketone (2.75 g.) (ketone content 60%), dissolved in 30 c.c. of petroleum ether, was stirred vigorously at room temperature for 1½ hours with 2.75 g. of KOH in 30 c.c. of water. The petroleum ether layer was separated and the alkaline layer was extracted with petroleum ether (15 c.c. × 2). After washing the extract with brine (15 c.c. × 2) and drying (Na_2SO_4), the solvent was removed (column) and the residue fractionated, b.p. 122°/12 mm, n_D^{25} 1.5130, d_4^{25} 1.019, yield 1.5 g ; $\lambda_{max}^{alc.}$ 237 mμ (ε 13,170). (Braude and Coles, *loc. cit.*, report : λ_{max} 237 mμ, ε 12,500 ; b.p. 114°/15 mm, n_D^{19} 1.5106).

The 2 : 4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method (crude ; m.p. 235-6°). Recrystallisation from benzene furnished dark red needles, m.p. 238° (decomp.). Mixed m.p. with an authentic sample (Sukh Dev, *loc. cit* , m.p. 244°) was 240°. (Found : N, 16.83. $C_{16}H_{18}O_4N_4$ requires N, 16.97%).

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N-SUBSTITUTED 2-AMINOTHIAZOLES AND THEIR ACETOXY-MERCURI DERIVATIVES

By P. N. Bhargava and M. Nagabhushanam

The acetoxymercuri derivatives of fifteen new N-substituted 2-arylaminothiazoles have been prepared. Reasons for the presence of acetoxymercuri group in the aryl nucleus attached to -NH group have been offered.

In view of the fungicidal activity of thiazole compounds the present investigation on the preparation of some new N-substituted 2-arylaminothiazoles was undertaken. It deals with the synthesis of a group of substituted thiazolylamines prepared by condensing acetophenone, acetone, ethyl acetoacetate and ethyl methyl ketone with *o*- and *p*-phenetyl- and *o*- and *p*-anisyl-thioureas in the presence of iodine according to the procedure of Dodson and King (*J. Amer. Chem. Soc.*, 1945, **67**, 2243), slightly modified. This method affords the advantage that different substituents including even hetero rings can be easily introduced at different positions of the thiazole nucleus, depending on the nature of the ketone or the ketonic ester taken.

All the fifteen N-substituted thiazolylamines have been mercurated with the expectation that mercury would enhance bactericidal activity. By allowing the N-substituted thiazolylamines to react with mercuric acetate, acetoxymercuri-thiazolylamines are formed. It is assumed that the acetoxymercuri group enters the aryl nucleus attached to NH group at position 2 or 4. Such an assumption is based on the fact that 2-acetylamino-4-methylthiazole, in which aromatic part is absent, does not undergo mercuration under the experimental conditions adopted in the present investigation, confirming thereby that the acetoxymercuri group does not enter the thiazole nucleus.

In view of the earlier observations on the mercuration of aromatic amines and phenols (Newton Friend, "Text Book of Organic Chemistry", Part I), it has been assumed that the acetoxymercuri group enters the *para* position with respect to NH group of the aryl nucleus in the thiazolylamine, and if the *para* position is blocked, substitution occurs at the *ortho* position. The general method for mercuration has been described in the Experimental.

The experimental procedure adopted for the preparation of N-substituted thiazolyl-amines has been illustrated in one special case in the Experimental.

EXPERIMENTAL

The substituted thioureas were prepared by the action of ammonium thiocyanate on the hydrochlorides of the corresponding bases (De Clermont, *J. Chem. Soc.*, 1877, **31**, 70).

4-Phenyl-2-o-phenetylaminothiazole.—A mixture of *o*-phenetylthiourea (13.1 g., 2*M*), acetophenone (4 g., 1*M*) and iodine (8.4 g., 1*M*) was heated under reflux for 8 hours on a water-bath and for another 12 to 16 hours without the use of a condenser. The period of heating influenced the yield of the final product. The crude reaction product was kept in contact with ether, with occasional stirring for 48 hours to remove the unchanged ketone, which otherwise led to a gummy product. Final removal of iodine was effected by treatment with sodium thiosulphate solution. The product was boiled with water to remove unchanged thiourea and filtered hot. The residue was treated with concentrated ammonia to liberate the base. Finally the base was purified by crystallisation from 30 to 60% alcohol three or four times. The properties and analytical data are recorded in Table I.

TABLE I

N-Substituted 2-aminothiazoles.

No.	Thiazole.	M.P.	Yield.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found.	% Sulphur. Calc.
1.	4-Phenyl-2-*o*-phenetylamino-	75°	89%	9.43	9.46	10.61	10.81
2.	4-Phenyl-2-*p*-phenetylamino-	102°	86	9.48	9.46	10.71	10.81
3.	4-Phenyl-2-*o*-anisylamino-	85°	84	9.91	9.93	11.49	11.34
4.	4-Methyl-2-*o*-phenetylamino-	67°	61	11.90	11.96	13.56	13.68
5.	4-Methyl-2-*p*-phenetylamino-	132°	64	11.89	11.96	13.61	13.63
6.	4-Methyl-2-*o*-anisylamino-	>280°	58	12.64	12.73	14.61	14.54
7.	4-Methyl-2-*p*-anisylamino-	104°	56	12.78	12.73	14.68	14.54
8.	4-Methyl-5-carbethoxy-2-*o*-phenetylamino-	80°	59	9.19	9.15	10.54	10.46
9.	4-Methyl-5-carbethoxy-2-*p*-phenetylamino-	94°	56	9.22	9.15	10.60	10.46
10.	4-Methyl-5 carbethoxy-2-*o*-anisylamino-	157°	61	9.60	9.58	11.07	10.96
11.	4-Methyl-5-carbethoxy-2-*p*-anisylamino-	133°	57	9.55	9.58	11.04	10.96
12.	4:5-Dimethyl-2-*o*-phenetylamino-	64°	52	11.32	11.29	11.48	11.50
13.	4:5-Dimethyl-2-*p*-phenetylamino-	76°	54	11.35	11.29	11.53	11.50
14.	4:5-Dimethyl-2-*o*-anisylamino-	125°	49	12.01	11.96	13.73	13.68
15.	4:5-Dimethyl-2-*p*-anisylamino-	91°	56	12.04	11.96	13.71	13.68

Mercuration of Thiazoles.—The thiazole (1*M*) in alcohol-dilute acetic acid solution was treated with an aqueous solution of mercuric acetate, acidified with acetic acid. The precipitate was obtained after some time. The reaction mixture was allowed to stand overnight. The product was filtered and purified by washing with hot water, alcohol and dilute acetic acid. The properties and analytical data are reported in Table II.

TABLE II

N-Substituted-2-o- or 2-p-acetoxymercuri (Acm) arylaminothiazoles.

No.	Thiazole.	M.P	Yield.	% Mercury. Found.	Calc.
1.	4-Phenyl-2-*p*-Acm-*o*-phenetylamino-	172°	79%	49.21	49.33
2.	4-Phenyl-2-*o*-Acm-*p*-phenetylamino-	193°	74	49.48	49.33
3.	4-Phenyl-2-*p*-Acm-*o*-anisylamino-	186°	80	50.43	50.20
4.	4-Methyl-2-*p*-Acm-*o*-phenetylamino-	176°	73	40.56	40.71
5.	4-Methyl-2-*o*-Acm-*p*-phenetylamino-	>280°	75	40.83	40.71
6.	4-Methyl-2-*p*-Acm-*o*-anisylamino-	138°	78	42.09	41.92
7.	4-Methyl-2-*p*-Acm-*p*-anisylamino-	214°	83	42.13	41.92
8.	4-Methyl-5-carbethoxy-2-*p*-Acm-*o*-phenetylamino-	192°	79	35.64	35.52
9.	4-Methyl-5-carbethoxy-2-*o*-Acm-*p*-phenetylamino-	236°	76	35.30	35.52
10.	4-Methyl-5-carbethoxy-2-*p*-Acm-*o*-anisylamino-	>280°	74	36.61	36.42
11.	4-Methyl-5-carbethoxy-2-*o*-Acm-*p*-anisylamino-	182°	81	36.54	36.42
12.	4:5-Dimethyl-2-*p*-Acm-*o*-phenetylamino-	132°	63	39.82	39.59
13.	4:5-Dimethyl-2-*o*-Acm-*p*-phenetylamino-	158°	66	39.69	39.59
14.	4:5-Dimethyl-2-*p*-Acm-*o*-anisylamino-	181°	64	40.91	40.78
15.	4:5-Dimethyl-2-*o*-Acm-*p*-anisylamino-	193°	69	40.91	40.78

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DITERPENE ALKALOIDS OF THE ROOT OF *INULA ROYLEANA* DC.

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The active constituents of the root of *Inula royleana* DC. (Fam. Compositae) consist chiefly of diterpene alkaloids, inuline, $C_{32}H_{46}O_8N_2$, m.p. 164° (decomp.), and methyl lycaconitine, $C_{37}H_{50}O_{10}N_2$, besides a few more basic ingredients as minor components. Another alkaloid, royline, $C_{25}H_{41}O_7N$, m.p. 134-35° (decomp.), which appears in larger quantities in lime-treated plant extract, has been shown to be an artefact of inuline, the latter suffering degradation to the former during processing with lime. From the studies of their physical, chemical and spectral properties, royline and inuline are proved to be identical with the diterpene alkaloid lycoctonine and its anthranoyld erivative respectively. The latter two occur in *Delphinium* and *Aconitum*, two closely related genera of Fam. Ranunculaceae. Thus, isolation of inuline and other diterpene alkaloids from Compositae reveals biogenetic interrelationship between these two plant families.

Inula royleana DC. (Fam. Compositae), a stout herb growing abundantly in Kashmir (7,000-11,000 ft), enjoys a favourable reputation in its habitat as a valuable medicinal plant. It is considered to be poisonous, disinfectant and insecticidal.

Preliminary chemical investigation of the root of this Indian *Inula* was first undertaken by Chopra, Kohli and Handa (*Indian J. Med. Res.*, 1945, **33**, 139). They isolated from this plant an alkaloid, *royline*, $C_{21}H_{33}O_6N$. Subsequent investigation by the present authors revealed the presence of another alkaloid having the empirical formula, $C_{16}H_{23}O_4N$, melting at a range of 158-61°, for which the name "inuline" was proposed (Chatterjee and Talapatra, *Proc. Indian Sci. Cong.*, 1957, Part III, p. 124). Recently Handa *et al.* have been successful in isolating inuline from the same source (*Indian J. Pharm.*, 1958, **20**, 211). Further chemical studies have led to the characterisation of these alkaloids which constitute the subject matter of the present communication.

An alcoholic extract of the powdered bitter root of *I. royleana* on concentration provided a deep brown viscous residue. It was treated with lime and extracted with ether, which on evaporation yielded a mixture of several alkaloids. Separation of these alkaloids, which contain inuline and royline besides several other basic components, has been successfully carried out by preliminary chromatographic resolution, followed by repeated fractional crystallisations. Fractional crystallisations of the perchlorates also provide a satisfactary method for their resolution. Counter-current distribution between benzene and buffer of *p*H 5 has been found to be a successful procedure for resolving the crude alkaloid mixture into inuline and five other basic ingredients.*

An interesting observation has been made during the isolation of inuline and royline from their crude alcoholic extract. The latter is found to occur in minute quantities (detectable by paper chromatography) in the alkaloid mixture when the alcoholic plant-extract is not pretreated with lime. Instead, an amorphous base appears

* This experiment was performed by Dr. O. E. Edwards, National Research Council, Ottawa, Canada, at the personal request of one of the authors (A.C.).

and it resists all attempts to crystallisation. It produces royline when subjected to hydrolytic fission with lime or strong alkali. This eventually shows that royline is an artefact of the amorphous base and is not a natural product.

Purity and homogeneity of inuline and royline have been established both by X-ray diffraction method and paper chromatography experiments. Pure inuline shows a single blue fluorescent spot (R_f 0.81) in presence of U.V. light, whereas royline exhibits only one Drangendorff positive spot (R_f 0.55), the mixture of butanol-acetic acid-water being used as developer.

Inuline, $C_{32}H_{46}O_8N_2$, crystallises from dilute alcohol in stout needles, with one molecule of solvent of crystallisation. The purest sample, which is chromatographically homogeneous, melts with a range of 160-64° (decomp.). It is optically active and *dextro*-rotatory, $[\alpha]_D^{30}$ + 44°.3 (chloroform). On the basis of elementary analyses of a number of samples, prepared under different conditions, inuline was suggested earlier to have the empirical formula, $C_{16}H_{23}O_4N$ (Chatterjee and Talapatra, *loc. cit.*) which has subsequently been confirmed by analyses of its various derivatives. Potentiometric titration suggests its weak monoacidic behaviour (pK, 8.25 in 80% alcohol) and corresponds to the double molecular formula, $C_{32}H_{46}O_8N_2$. It combines with a few acids to form crystalline salts. Thus, it yields a perchlorate, $C_{32}H_{46}O_8N_2.HClO_4$, decomposing above 210°, although the chloroplatinate, decomposing above 270°, analyses for $C_{32}H_{46}O_8N_2.H_2PtCl_6$. Molecular weight obtained by potentiometric titration also agrees with the C_{32} formula, but that by the chloroplatinate or Rast's method does not appear to be satisfactory. The base forms an amorphous chloroaurate (aurichloride) decomposing above 200°, but its consistent analytical data have not been obtained. Other salts of inuline, e.g. hydrochloride, nitrate, picrate, oxalate, etc. could not be prepared as yet in a crystalline state.

Inuline reacts with Dragendorff's reagent to produce a reddish orange complex. It shows a beautiful blue-violet fluorescence in various solvents. The base does not exhibit any characteristic colour reaction with mineral acids and other alkaloidal reagents like Fröhde, Hopkin-Cole and Keller reagents. With concentrated sulphuric acid and potassium dichromate (Otto reaction) it develops a green colour and with concentrated sulphuric acid and ceric sulphate it turns pink. On warming with concentrated sulphuric acid and gallic acid it turns deep green which immediately changes to blue and finally to brilliant royal blue, thus showing positive Labat test although it does not form any red water-insoluble phloroglucide according to the method of Clowes-Tollens (Meyer, "Analyse und Konstitutions Mittelung", 1931, p. 496). Subsequent elucidation of the structure of inuline (II) shows the absence of methylenedioxy group in its molecule. It is, however, difficult at this stage to explain why inuline shows positive Labat test when methylenedioxy group is absent. Zeisel's experiment demonstrates the presence of four methoxyl groups. It carries one *N*-ethyl function (Herzig-Meyer's method, vide Experimental) which during the Kuhn-Roth oxidation produces acetic acid in molar proportion, thus explaining the presence of one C-methyl function in inuline molecule. The presence of three active hydrogen atoms has been indicated by Zerewitinoff's method.

The ultraviolet absorption spectrum of inuline studied in 95% ethanol exhibits sharp absorption maxima at 219 (log ϵ, 4.17), 249 (log ϵ, 3.64) and 339-40 mμ (log ϵ, 3.47) and absorption minima at 237 (log ϵ, 3.52) and 271 mμ (log ϵ, 2.36). The infra-red absorption spectrum in chloroform shows strong absorption peaks at 2.88 (O-H), 2.98 (>N-H), 5.91 (ester), 6.15 and 6.26 (benzene duplet), 6.37 and 6.74 (aromatic), 7.24 (C-Me) and 9.0μ (ether bridge, —C—O—R).

O

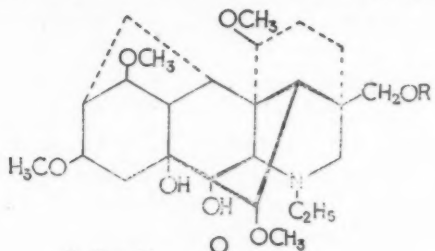
Inuline on catalytic reduction does not show any uptake of hydrogen, indicating that the base is probably saturated. With acetic anhydride and pyridine it forms a gummy mass which cannot be induced to crystallisation from any organic solvent. On refluxing in methanol with 50% KOH for 8 hours, inuline has been found to undergo hydrolytic fission to produce royline, $C_{25}H_{41}O_7N$, m.p. 133°, and anthranilic acid, $C_7H_7NO_2$, m.p. 146-47°, thereby proving that inuline is anthranoyl-royline. Inuline, however, resists hydrolysis under mild conditions, viz., in alcoholic solution with *N*-aqueous alkali at reflux temperature.

Royline, which is obtained from alkali hydrolysates of inuline, crystallises from dilute methanol in thin elongated needles with one molecule of water of crystallisation. The hydrated base sinters at 121-23° and melts at 132-33° (decomp.). On drying under reduced pressure at 80° for a long period, it changes to a transparent glassy mass; the powdered amorphous substance sinters at 120°, fuses at 128°, melts at 133-35° (decomp.) and evolves gas at 137°. Royline is *dextro*-rotatory having $[\alpha]_D^{27}$ + 51° (*c*, 1.7 in alcohol) and not *laevo*-rotatory which was earlier reported by Chopra and Handa (*loc. cit.*). The analytical figures now obtained for both the hydrated and anhydrous royline as well as for some of its salts correspond to the molecular formula $C_{25}H_{41}O_7N$ for the base. It is a monoacidic tertiary base and combines with a number of acids to produce crystalline salts. It forms colorless needles of hydroiodide, $C_{25}H_{41}O_7N.HI$, m.p. 185° (decomp.), from acetone. The perchlorate, $C_{25}H_{41}O_7N.HClO_4$, m.p. 206° (decomp.), separates from alcohol-ether in colorless prisms and the picrate, obtained as needles from ether-acetone melts at 156-58° (decomp.) and analyses for $C_{25}H_{41}O_7N.C_6H_3O_7N_3$. Standard analytical procedures indicate the presence of four methoxyl, one N-ethyl and three active hydrogens. Like inuline, which is presumably anthranoylroyline, royline also responds to the Labat test showing the same sequence of colour, but does not form any red phloroglucide.

The ultraviolet absorption spectrum of royline in 95% ethanol has no absorption maximum or minimum but only low end-absorption. The infra-red spectrum (in chloroform) shows strong absorption peaks at 2.93 (O-H), 6.80, 8.90, 9.17, 10 0, 10.50 and 11.6μ and severel peaks in the region of 7-8.4μ, thus lacking the absorptions at 2.98 (>N-H), 5.91 (ester) and 6.15, 6.26, 6.37, 6.74μ (aromatic), discernible in the infra-red spectrum of inuline. These are attributed to the anthranilic ester moiety present in the latter.

The low end-absorption in the ultraviolet spectrum of royline, the absence of peaks due to unsaturation in its infra-red spectrum, its failure to undergo catalytic hydrogenation, together with an examination of its molecular formula indicate that the base is a

saturated hexacyclic compound. Impressed by the similarity between royline and the diterpene alkaloid*, lycoctonine, having the same molecular formula $C_{25}H_{41}O_7N$ (Edwards, Marion and Stewart, *Canad. J. Chem.*, 1956, **34**, 1315 et seq.), the identity of these two bases is emphasised. Since inuline is anthranoylroyline, it must therefore be anthranoyllycoctonine. Identity of these compounds has been finally established by direct comparison. The chemistry and reactions of lycoctonine and its derivatives have recently been interpreted by Edwards *et al.* (*loc. cit.*) using structure (I) or its mirror image from an X-ray analysis by Przybylska and Marion (*ibid.*, 1956, **34**, 185). Royline and inuline therefore possesses structur (I) and (II) respectively.



Structure (I) for lycoctonine, as suggested earlier by Edwards (*loc. cit.*), awaits further confirmation. Edwards believes that this structure needs modification, details of which will appear soon (personal communication from Dr. O.E. Edwards, Ottawa, Canada).

Lycoctonine was first obtained by hydrolysis of lycaconitine, an alkaloid of *Aconitum lycoctonum* (Schulze and Bierling, *Arch. Pharm.*, 1913, **251**, 8) and has subsequently been isolated from a number of species of the two closely related genera, *Delphinium* and *Aconitum* of the same plant family, Ranunculaceae. Although lycoctonine has occasionally been found to occur in the free state, e.g. in *D. consolida* L. (Marion and Edwards, *J. Amer. Chem. Soc.*, 1947, **69**, 2010), it generally occurs as an ester of anthranilic acid, the amino group of the latter being further linked up as amide, (*a*) with succinic acid in some *Aconite* bases, e.g. in lycaconitine (Schulze and Bierling, *loc. cit.*) or (*b*) with methylsuccinic acid, as in methyllycaconitine (Manske and Marion, *Canad. J. Res.*, 1946, **B24**, 1; Goodson, *J. Chem. Soc.*, 1944, 108) or (*c*) with acetic acid, as in ajacine (Goodson, *loc. cit.*).

The occurrence of anthranoyl lycoctonine, an *Aconitum* alkaloid of Ranunculaceae family (N.O. Ranales) in Compositae family (N.O. Asterales) is thus recorded for the first time. This suggests their close biogenetic relationship. According to Hutchinson ("British Flowering Plants," 1948, p. 25) the order Asterales is evolved from Ranales through the Orders Carophyllales, Gentianales and Campanulales. This stands in favour of the idea that closely related plants are also close in their chemical make-up (Gibbs, *J. Linnean Soc.*, London, 1958, Zool. Vol. 44 and Bot. Vol. 56, p. 50).

* A comprehensive review on the *Aconite-garrya* alkaloids having diterpene-like skeleton has been published by Wiesner and Valenta "Progress in the Chemistry of Organic Natural Products", 1958, Vol. 16, pp. 26-89; ed. by Zechmeister and Published, by Julius-Springer, Vienna).

From the experiments studied so far and from biogenetic considerations, it seems that the amorphous base (*vide supra*) (accompanying inuline in *I. royleana*), the complete structure of which is yet to be elucidated, might have lycaconitine, methyl lycaconitine or ajacine like structure in which the amino group of the anthranilic acid moiety is present as amide*.

EXPERIMENTAL

Extraction of Inula royleana D.C.—The extremely bitter, dried and powdered root (2 kg.) of *I. royleana* D.C. was soaked in a percolator with 95% ethanol (16 litres) for a week. The reddish brown alcoholic extract was drained out and the drug was repeatedly extracted with alcohol by percolation. The combined alcoholic extract was concentrated under reduced pressure on a water-bath to about 200 c.c. The thick brown concentrate was divided into two equal parts (A & B). The first part (A) was poured in sufficient quantity of 3*N*-HCl with continuous stirring to exhibit an acid reaction to Congo-red and kept overnight. The supernatant liquid was decanted from the separated non-basic resinous mass and the acid aqueous portion was basified with ammonium hydroxide and exhaustively extracted with chloroform. The combined chloroform extract was freed of solvent by distillation under reduced pressure; the crude basic residue having brown thick syrupy consistency weighed 47 g.

The crude alkaloid was dissolved in minimum quantity of 2*N*-HCl, treated with an excess of aqueous sodium bicarbonate (*p*H 7.0-7.5) and thoroughly extracted with chloroform (extract C). The solution was then basified with an excess of ammonia and extracted with chloroform (extract L).

Chloroform extract (C), containing the weak bases, was extracted with *N*-HCl. The bases forming chloroform-soluble hydrochlorides remained in chloroform layer (C_1) and the rest in the aqueous phase. The latter was then basified with ammonium hydroxide and extracted with ether (C_2).

The chloroform extract (L) was similarly treated to yield fraction (L_1) (containing chloroform-soluble base hydrochlorides), fraction (L_2) (containing other soluble bases) and fraction (L_3) (containing chloroform-soluble bases).

The method of separation into different fractions is outlined in Chart I.

Fraction (C_1) was washed with dilute ammonia and water, distilled and the residue obtained neither crystallised nor produced any salt.

Each of the fractions (L_1), (L_2) and (L_3) responded positive to the Dragendorff test for alkaloid, but from these only oily or gummy basic residues were obtained in poor yields. Presence of royline in fractions (L_2) and (L_3) was indicated by paper chromatography.

Isolation of Inuline from the Fraction (C_2).—The ether extract (C_2) exhibiting a strong blue-violet fluorescence was distilled to dryness to leave a reddish brown gum. A part (major) was dissolved in *N*-H_2SO_4 and basified with aqueous sodium bicarbonate solution (*p*H 7). The separated white flocculent base was taken up in ether; the ether extract was dried and concentrated. The residue was dissolved in benzene (40 c.c.) and chromatographed through a column of alumina (40 cm × 2.5 cm).

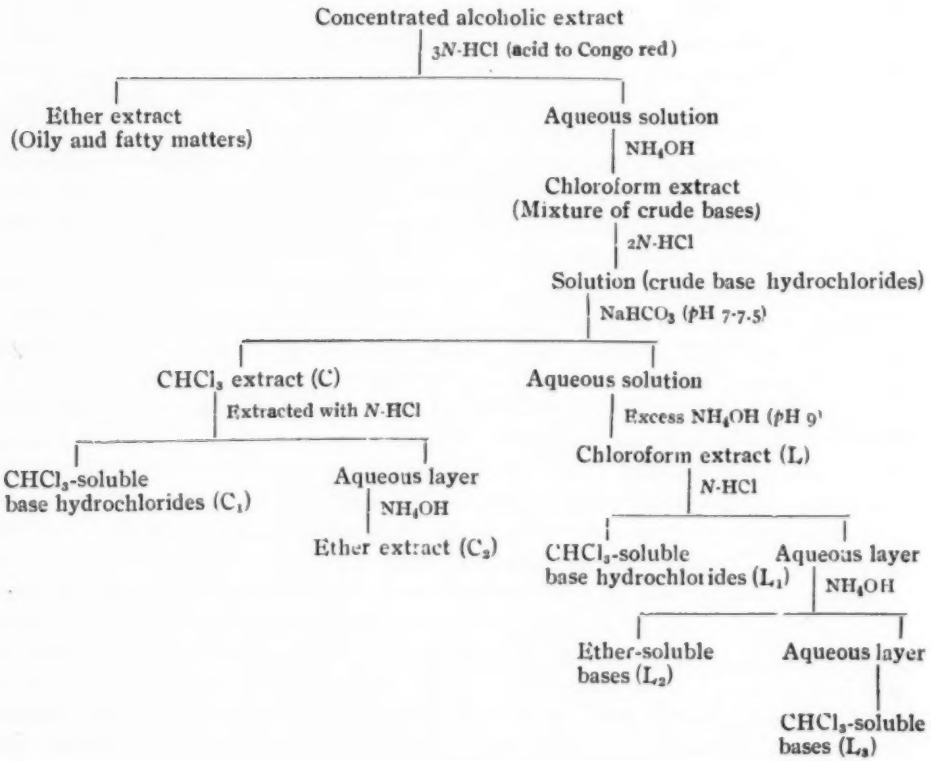
*Further investigation has established its identity with methyl lycaconitine, $C_{37}H_{50}O_{10}N_2$ (Goodson, *loc. cit.*).

The column was first eluted with benzene, then with a mixture of benzene and acetone in different proportions and the eluates were collected in fractions of 30 c.c. each (Table I).

TABLE I

Eluents.	Fractions collected.	Residue on evaporation.
Benzene	1—2	Nil
Benzene : acetone (8 : 2)	3—5	Uncrystallisable glassy residue,
Benzene : acetone (5 : 5)	6—10	Solid residue, m p. 145-50°
Benzene : acetone (5 : 5)	11—12	Nil

CHART I



The fractions (6-10) could be crystallised from dilute ethanol to yield *inuline* in thick needles, m.p. 155-60° (decomp.) (1.8 g. approx.). Inuline was purified by several recrystallisations from dilute ethanol when shining heavy needle-shaped crystals, m.p. 160-64° (decomp.), were obtained. For analysis, a pure sample was dried under

vacuum over P_2O_5 at 80° for 20 hrs. [Found: C, 65.12, 64.82, 64.91; H, 7.98, 8.16, 7.88; N, 4.85, 4.92; O, 22.93, 22.62; $-OCH_3$, 20.74, 20.92; $N.C_2H_5$, 5.64, 5.34 (cf. royline, *vide infra*); $C-CH_3$, 2.46; H^+, 0.65. $C_{32}H_{46}O_8N_2$ requires C, 65.52; H, 7.85; N, 4.78; O, 21.84; 4-OCH_3, 21.12; 1 N-C_2H_5, 4.94; 1 C-CH_3, 2.57; $3H^+$, 0.51%. $C_{30}H_{46}O_8N_2$ requires C, 64.06; H, 8.19; N, 4.98; O, 22.78; 4-OCH_3, 22.06; 1N-C_2H_5, 5.16; 1C-CH_3, 2.66; $3H^+$, 0.54%].

Inuline is freely soluble in pyridine and *NN*-dimethylformamide, moderately soluble in chloroform, acetone and benzene, sparingly in hot ethanol and methanol, slightly so in these solvents in the cold and in ether, and very slightly soluble in petroleum ether and water. It exhibits a strong violet fluorescence in dilute solutions. A very dilute solution of inuline in water tastes extremely bitter. Fractions (3-5) could not be crystallised from any solvent and the amorphous solid melted with a range and could not be prepared homogeneous.

Potentiometric Titration of the Base.—A solution of inuline (0.0267 g.) in 80% alcohol consumed 4.5 c.c. of 0.1*N*-HCl when titrated potentimetrically; M.W. 594; *pK*, 8.25. Only one inflection was observed in the titration curve, showing the monoacidic nature of the base. $C_{32}H_{46}O_8N_2$ requires M.W. 586.

Inuline chloroplatinate was obtained as a yellow precipitate by adding an aqueous solution of platinum chloride (5%) to a solution of inuline (0.1 g.) in minimum amount of HCl (dil.) until precipitation was complete. It was highly soluble in alcohol. The salt was purified by several crystallisations from water containing a few drops of HCl (dil.), when fine yellow needles of the *chloroplatinate*, which decomposed above 270° without melting, were obtained. [Found in a sample dried under vacuum over P_2O_5 at 135° for 24 hours: C, 37.88; H, 4.79; N, 2.42. $C_{32}H_{46}O_8N_2.H_2PtCl_6$ requires C, 38.55; H, 4.89; N, 2.81%; M.W. 586. $C_{30}H_{46}O_8N_2.H_2PtCl_6$ requires C, 37.03; H, 4.94; N, 2.88%; M.W. 562]. Inuline chloroplatinate (6.043 mg.) after combustion yielded a residue (1.235 mg.) corresponding to the molecular weight of the base as 540.

Inuline Chloroaurate.—To a solution of pure inuline (0.1 g.) in HCl (very dilute) a solution of pure gold chloride (5%) was added dropwise till complete precipitation. The orange-yellow *chloroaurate*, m.p. 200° (decomp.), was filtered, washed with distilled water and dried. It could not be crystallised since it suffered decomposition during concentration of its solution. (Found in a sample dried over P_2O_5 at 130° for 20 hours: C, 32.97; H, 4.14; N, 2.67. $C_{32}H_{46}O_8N_2$, $2HAuCl_4$ requires C, 30.33; H, 3.79; N, 2.22%).

Inuline Perchlorate.—A solution of the base (0.1 g.) in absolute methanol was neutralised with 65% perchloric acid and the *perchlorate* formed separated out from methanol and dry ether as a crystalline solid. The compound darkens at above 155°, decomposes and clears gradually above 210° without melting. It was purified by several crystallisations. (Found in a dry sample: C, 56.31; H, 7.01; N, 3.87. $C_{32}H_{46}O_8N_2.HClO_4$ requires: C, 55.94; H, 6.85; N, 4.08%).

Isolation of Inuline and the Amorphous Base from (C_2).—The reddish brown basic gum (C_2) was dissolved in alcohol and acidified with excess of 67% perchloric acid.

The brown solution on keeping gradually deposited a good amount of perchlorate of a base in amorphous state. The solution was allowed to stand overnight and then filtered. The filtrate (D) on addition of excess of ammonia and extraction with ether yielded the base, inuline, m.p. 153-56°. It was purified by repeated crystallisations from 90% ethanol when heavy needles, m.p. 162-64° (decomp.), were obtained. The filtrate (D) also deposited inuline perchlorate on dilution with large a volume of water.

The amorphous perchlorate was crystallised with difficulty from dilute alcohol to yield fine colorless needles, m.p. 185° (decomp.). The base liberated from the perchlorate by addition of excess ammonia to its suspension in water was an amorphous solid, fusing at 112-19° and decomposing above 140°. It is highly soluble in most of the solvents, but slighly soluble in petroleum ether. It was not a homogeneous substance as examined from its paper chromatogram. On heating with strong aqueous alkali it yielded royline. Attempts to prepare a homogeneous sample of this base and further studies on its nature are in progress*.

Isolation of Inuline and Royline from Crude Alcoholic Extract Pretreated with Lime.—The portion (B) (*vide supra*) of the alcoholic concentrate of the plant materials was thoroughly mixed with lime (equal amount by weight) and kept overnight. Next morning the solid mass was powdered and soxhletted with ether. The ether extract was washed with water, dried and concentrated to yield a sticky gelatinous substance as a residue. It was dissolved in minimum quantity of chloroform and the chloroform solution was exhaustively extracted with 2*N*-HCl. The chloroform extract was washed with ammonia and distilled to furnish a little uncrystallisable oily residue (Dragendorff's test, positive). The acid aqueous solution was treated with an aqueous sodium bicarbonate (*p*H 6.5-7) and extracted several times with ether (extract B_1). The solution was then treated with an excess of ammonia and extracted thoroughly with chloroform (extract *M*).

Inuline from (B_1).—The ether extract (B_1) was washed, dried and concentrated, as usual, to yield a glassy residue. It was dissolved in benzene and chromatographed through Brockmann alumina (neutral) as before. Benzene : acetone (8 : 2) eluate (3 fractions, 10 c c.) yielded a glassy sticky residue (0.4 g.) which could not be crystallised. The later fractions (4 fractions, 120 c.c.), eluted by benzene : acetone (5 : 5), crystallised from 90% alcohol to yield needles of inuline, m.p. 150-55° (decomp.) (0.45 g.). This was purified by several crystallisations from dilute alcohol when colorless stout needles of inuline, m.p. 164-66° (decomp.) were obtained.

Royline from (*M*).—The chloroform extract (M) was washed with water and concentrated ; the transparent pale brown sticky residue was dissolved in benzene and subjected to chromatographic resolution over aluminia (40 cm × 2.5 cm). The six fractions (180 c.c.) eluted by benzene : acetone (8 : 2) on evaporation yielded a

*Homogeneous sample of the base, now obtained, has been found to be identical with methyl lycaconitine, $C_{37}H_{50}O_{10}N_2$, from analyses and hydrolysis experiments (Goodson, *l c. cit*). The same observation has recently been recorded by Valenta *et al.* (*Chem. & Ind.*, 1959, 513).

gummy mass. The latter was dissolved in 90% methanol. The solution while standing overnight deposited a crystalline base royline, which was recrystallised from the same solvent in colorless needles with one molecule of water of crystallisation, m.p. 134-35° (decomp.) (started fusing at 123-24°), total yield 7.5 g., $[\alpha]_D^{25}$ + 51° (*c*, 1 7% in alcohol). The *hydrated base* on drying at 80°/20 mm for 24 hours lost water corresponding to one molecule and became an amorphous glassy mass. The powdered amorphous substance fuses at 123° and melts at 133-35° (decomp.) with evolution of gas at 137°. (Found in a pure hydrated sample: C, 62.03; H, 8.69; N, 3.01. $C_{25}H_{41}O_7N$, H_2O requires C, 61.86; H, 8.87; N, 2.89%. [Found in a pure anhydrous sample: C, 63.93; H, 8.78; N, 3.29; O, 24.29; H^+ (in anisole), 0.59; C-CH_3, 2.91; equiv. (titration with *N*/5 HCl potentiometrically) 474. $C_{25}H_{41}O_7N$ requires C, 64.24; H, 8.78; N, 3.00; O, 23.98; $3H^+$, 0.63; 1C-CH_3, 3.21%; equiv., 467].

Royline hydrate (0.15 g.) was submitted to the usual Herzig-Meyer N-alkyl determination, the gas evolving during pyrolysis of the base hydroiodide was passed into a cold solution of trimethylamine in methanol. The solution on concentration yielded fine needles of ethyltrimethylammonium iodide (10 mg.), m.p. 315° (decomp.); mixed m.p. with an authentic sample (having m.p, 317°, decomp.) remained undepressed. Royline is highly soluble in alcohol, acetone and chloroform, but soluble in ether and very slightly soluble in petroleum ether.

Royline Hydroiodide.—A solution of royline (0.1 g.) in acetone was made just acidic by careful addition of freshly distilled colorless hydroiodic acid. On concentration, colorless needles of *royline hydroiodide*, m.p. 185° (decomp.), separated. The salt was purified by several crystallisations from acetone. (Found in a dry sample: C, 50.33; H, 7.05; N, 2.52. $C_{25}H_{41}O_7N$. HI requires C, 50.42; H, 7.11; N, 2.35%).

Royline Perchlorate.—A solution of royline (0.1 g.) in minimum amount of methanol was made just acid to Congo red by careful addition of 65% perchloric acid. The dropwise addition of absolute ether to the solution effected the separation of the crystalline *perchlorate*. It was recrystallised from methanol-ether in colorless prisms, m.p. 206° (decomp.), when immersed in the bath at 185°. (Found in a dry sample: C, 53.42; H, 7.31; N, 2.23. $C_{25}H_{41}O_7N.HClO_4$ requires C, 52.85; H, 7.4; N, 2.47%).

Royline picrate was crystallised with difficulty from ether-acetone mixture as yellow needles, melting at 156-58° (decomp.). (Found in a pure dry sample: C, 52.91; H, 6.64. $C_{25}H_{41}O_7N.C_6H_3O_7N_3$ requires C, 53.44; H, 6.32%).

Homogeneity of Inuline and Royline by Paper Chromatography.—Alcoholic solutions (0.1 c.c.) of the pure bases and their mixtures (2-7 mg./c.c.) were applied on Whatman

TABLE II

Substance.	Conc.	*Rf* value.	Remark.
(*a*) Inuline m.p. 164°	3.4 mg./1.5 c.c.	0.81	Fluorescent under U.V. but not positive to Dragendorff's reagent.
(*b*) Royline m.p. 134°	7.1 mg /c.c.	0.55	Dragendorff positive.
(*c*) Mixture of inuline and royline		0.81	Corresponding to inuline.
		0.55	Corresponding to royline.

No. 1 paper and subjected to unidimensional paper chromatography by employing the ascending technique. Chromatograms were developed using *n*-butanol-acetic acid-water (10 : 1 : x, where x is the quantity of water required to saturate the mixture of butanol and acetic acid) as the solvent mixture. The results obtained are recorded in Table II.

Attempted Preparation of Phloroglucide from Inuline.—The phloroglucinol solution was prepared, as usual, by warming phloroglucinol (1 g.) with a mixture of H_2SO_4 (conc., 33 g.) and water (40 g.), keeping the mixture for an hour and then decanting the supernatant solution from any insoluble matter.

Inuline (0.1138 g.) was treated with water (5 c.c.) and phloroglucinol solution (30 c.c.) and warmed for 2 hours at 70-80°. No turbidity appeared* even after long heating or boiling and no precipitate separated even after keeping for 24 hours. An orange-red crystalline solid appeared only when the solution was thoroughly cooled in a freezing mixture. But unlike phloroglucide* it was highly soluble in water.

Attempted Alkali Hydrolysis of Inuline (under mild conditions).—Inuline (0.5 g.) was heated on a water-bath with alcohol (5 c.c.) and aq. *N*-NaOH (1.5 c.c.) until the alcohol had evaporated. Needle-shaped solids of unchanged inuline began to separate while concentrating. The residue was treated with 5 c.c. of water and cooled, when more needles separated. The solid (0.45 g.), m.p. 155-59°, showed no depression in melting point while admixed with inuline.

Hydrolysis of Inuline with Strong Alkali: Isolation of Royline.—A solution of inuline (0.45 g.) in methanol (5 c.c.) was heated on a steam-bath with a 50% aqueous solution of KOH (1 g. in 1 c.c.) for 12 hours. The solution was then diluted with water (5 c.c.) and gently heated on a water-bath ; when almost all methanol had evaporated off, a base began to separate in the form of oil drops. It was cooled in ice when colorless, needle-shaped crystals (0.31 g.) began to separate on scratching. The solid was filtered (the filtrate F, kept aside) and purified by recrystallisation from dilute methanol in the form of fine needles (with a molecule of water as solvent of crystallisation), m.p. 133-35° with previous sintering at 124°. The compound was found to be identical with royline with which it showed no depression in m.p.

The hydrated needles of royline loses one molecule of water of crystallisation on drying at 80°/20 mm for 20 hours and becomes an amorphous glassy mass. (Found in a dry sample : C, 64.01 ; H, 8.69. Calc. for $C_{23}H_{41}O_7N$: C, 64.24 ; H, 8.78%).

Isolation of Anthranilic Acid.—The aqueous alkaline filtrate (F) was extracted with ether to remove traces of royline or unchanged inuline ; the solution was rendered just acid with dilute hydrochloric acid (*p*H 3-4) and filtered from a small amount of amorphous precipitate. The filtrate was repeatedly extracted with ether (20 c.c. × 6), the combined extract was washed with water, dried and concentrated. The residue was crystallised from a mixture of ether-petroleum ether (b.p. 60-80°) in fine pale yellow heavy needles (0.05 g.), m.p. 145°, which were purified by several recrystallisations from the same solvent mixture ; the m.p. (146-47°) of the pure crystals was undepressed

* Under identical condition beautiful orange-red crystalline phloroglucide was obtained quantitatively from berberine, and the phloroglucide, very slightly soluble in water, began to separate as soon as the substance was heated with the phloroglucinol solution.

when admixed with anthranilic acid. (Found in a dry sample: C, 61.44; H, 5.01; N, 10.34. Calc. for $C_7H_7O_2N$: C, 61.31; H, 5.11; N, 10.22%).

Catalytic Hydrogenation of Royline and Inuline.—A solution of royline in alcohol or 2*N*-HCl did not consume any hydrogen in presence of Adams platinum oxide or palladised-charcoal catalyst, and in each case the base was recovered unchanged. The same behaviour was shown by inuline.

Alkali Fusion of Royline.—Royline (1 g.) was fused with KOH (6 g.) in a nickel crucible at 300-305° (metal bath temperature) and kept for about 10 mins. until copious evolution of fumes with a characteristic odour had ceased. The melt gradually changed its colour from red to brown and finally to black. The cooled mass was poured in water, filtered, thoroughly cooled and extracted with ether (extract K_1).

From the aqueous layer, an acidic fraction (red oil) was obtained which did not furnish any solid on high vacuum sublimation. The extract (K_1) was separated into a basic and a neutral fraction in the usual way, neither of which gave any solid product even after high vacuum sublimation. The basic fragment highly smelt of *pyridine* but could not be characterised due to paucity of materials.

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SHORT NOTES

1-(*O*-CARBETHOXYPHENYL)-3-(SUBST.)-PHENYLTHIOUREAS

By K. J. Shah and J. J. Trivedi

Shimotani (*J. Pharm. Soc., Japan*, 1952, **72**, 328) has shown that carbethoxyphenylthioureas exhibit a vermicidal activity similar to *n*-hexylresorcinol on earthworms. Several mono- and di-substituted thioureas exhibit a variety of physiological properties (Huebner, *J. Amer. Chem. Soc.*, 1953, **75**, 2274 ; Doub *et al.*, *ibid.*, 1958, **80**, 2205 ; Buu Hoï, *Internat. J. Leprosy*, 1954, **22**, 16 ; *Compt. rend.*, 1954, **238**, 2582). In order to study their physiological properties several 1-(*O*-carbethoxyphenyl)-3-(substituted phenyl)-thioureas have been prepared.

The preparation of *iso*thiocyanates and their condensation with ethyl anthranilate to obtain 1-(*O*-carbethoxyphenyl)-3-(subst.-phenyl)-thioureas were carried out as described by Trivedi *et al.* (this *Journal*, 1956, **33**, 423 ; 1958, **35**, 657). Compounds prepared are described in Table I

Table I

(O)-EtO.OC.C_6H_4-NHCSNHC_6H_4..X

No	Substituent X.	Mol. formula .	Cryst app.	M.P.	%Sulphur. Found.	Calc.
1.	*o*-CH_3	$C_{17}H_{18}O_2N_2S$	Granules	255°	9.9	10.2
2.	*p*-CH_3	,,	Small needles	157°	9.8	10.2
3.	*m*-CH_3	,,	Grains	273°	10.0	10.2
4.	*o*-OCH_3	$C_{17}H_{18}O_3N_2S$	Do	267°	9.5	9.7
5.	*p*-OCH_3	,,	Plates	138°	9.4	9.7
6.	*m*-Cl	$C_{16}H_{15}O_2N_2ClS$	Grains	290°	9.3	9.6
7.	*p*-Cl	,,	Needles	332°	9.4	9.6
8.	*m*-Br	$C_{16}H_{15}O_2N_2BrS$	Plates	291°	8.1	8.4
9.	*p*-Br	,,	Grains	295°	8.3	8.4

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VOLUMETRIC ESTIMATION OF THIOUREA IN PRESENCE OF MERCURIC CHLORIDE

By Satyendra Nath Banerjee

The oxidation of thiourea to disulphide $[NH_2(NH)CS]_2$ has been used for the determination of chromate, chlorate, bromate, manganese dioxide, lead peroxide and many per-compounds (Mahr and Ohle, *Z. anal. Chem.*, 1939, **117**, 389; *Z. angew. Chem.*, 1939, **52**, 238, 618). Mahr (*Z. anal. Chem.*, 1939, **117**, 91) employed $KBrO_3$-KBr solution as the titrant for the volumetric estimation of thiourea in presence of sulphuric acid and potassium iodide at 35° with starch as indicator. Mahr (*loc. cit.*) mentioned that copper and mercury salts caused trouble.

In the present work with a view to estimating thiourea in presence of mercuric chloride, the method of Mahr has been repeated and its conditions modified. Experimental condition for the estimation of thiourea in presence of varying amounts of mercuric chloride has also been investigated.

Estimation of Thiourea.—Approximately 0.2*N*-thiourea solution (10 c.c.) was mixed with about 15 c.c. of 18*N*-H_2SO_4 and about 10 c.c. of 1%KI solution. The mixture was then diluted to an approximate volume of 80 c.c. and 1-2 c.c. of starch solution was then added. It was titrated dropwise with constant shaking against a standard $KBrO_3$-KBr solution until a blue colour of starch iodide was formed. Now, after diluting to about 200 c.c., a dropwise titration was continued, if required, until a sharp blue colour appeared.

From a study of the effect of variation of different factors on the estimation of thiourea, it has been observed that both greater (20 c.c. of 18 *N* or more) or lesser (5 c.c. of 18 *N* or less) amounts of sulphuric acid produce high results. Similar observation has been noted at elevated temperature with no additional advantage whatsoever. It has also been found that dropwise titration with 10 c.c. of 1% KI solution provides most accurate result.

Estimation of Thiourea in presence of Mercuric Chloride Solution.—From a study of the effect of variation of H_2SO_4 and KI solutions in the estimation of appoximately 0.2*N*-thiourea solution in presence of 1 c.c. of $HgCl_2$ solution (10 g. of $HgCl_2$ in 250 c.c. water) by titration with a standard $KBrO_3$-KBr solution at room temperature, it has been observed that the optimum amounts of 18*N*-H_2SO_4 and of 1% KI solution to be added are 10-15 c.c. in both cases. With increase in the amount of $HgCl_2$ solution, the amount of KI solution to be added is to be increased. The formation of red or yellow precipitate during titration shows the deficiency in the amount of KI solution in the mixture, which can be overcome by adding more of KI solution before further completion of the titration. Hence, a larger amount of KI should always be added which probably keeps mercury in solution as the complex ion, HgI_4^{2-}, thus enabling the estimation of thiourea possible in presence

of mercuric chloride. Higher concentration of sulphuric acid may be detected by the appearance of a yellow precipitate at the initial stage of titration, which should be avoided. With lesser amount of sulphuric acid, no permanent blue end-point is reached, even if it be over.

The titration may be carried out with the same accuracy, in one-stage, after diluting the solution mixture to about 200 c.c. at the beginning; but two-stage titration, as done here, is preferable since it offers a good guidance in the detection of sharp blue end-point.

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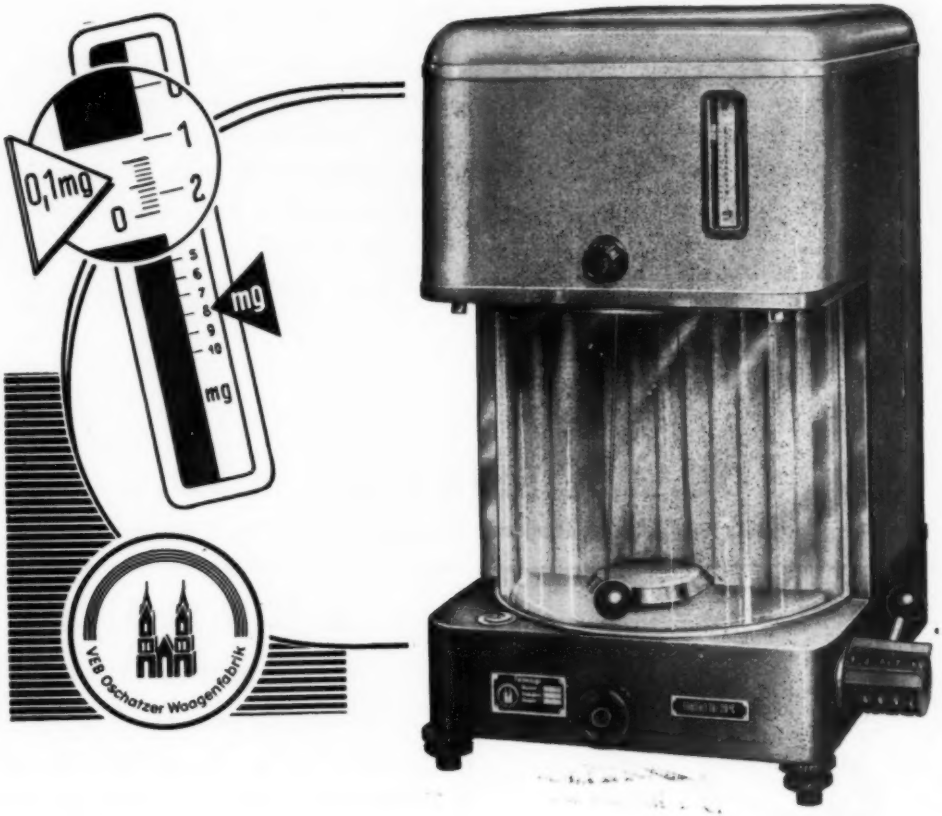

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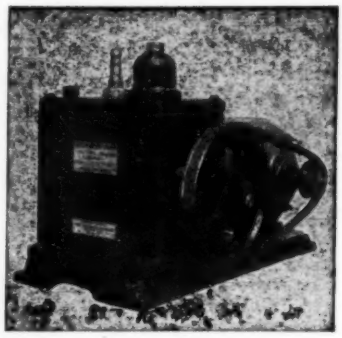

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